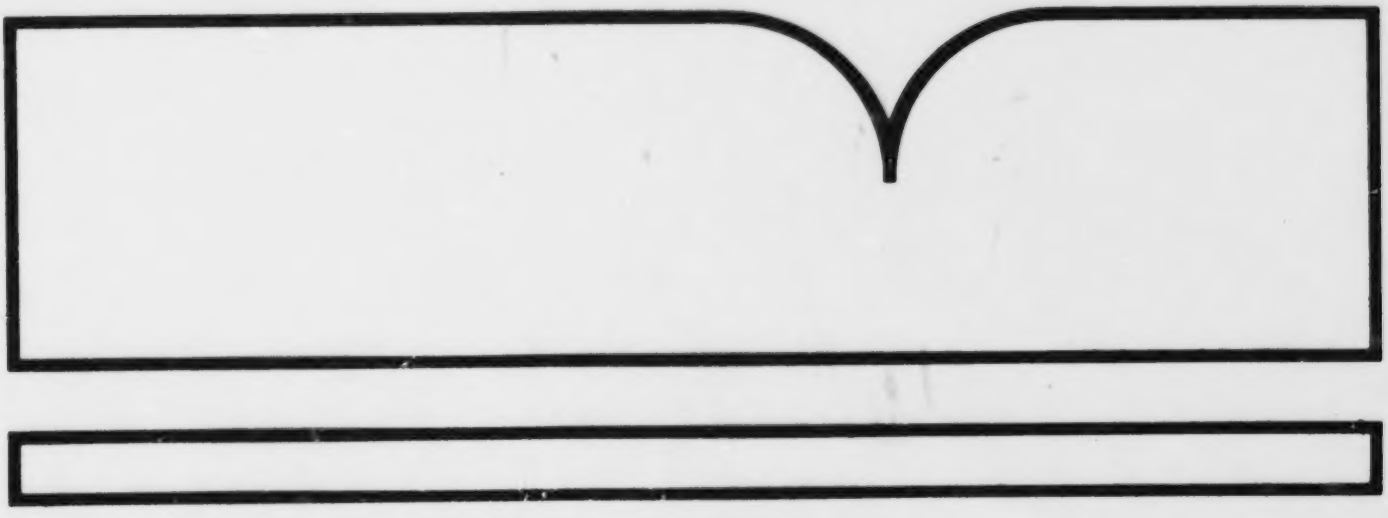
PB84-129014

Stone Deterioration Studies at the Bowling Green Custom House, 1980-1981

(U.S.) Environmental Protection Agency
Washington, DC

Jan 84



U.S. Department of Commerce
National Technical Information Service
NTIS

PB84-129014

EPA-600/6-84-003
January 1984

STONE DETERIORATION STUDIES AT THE BOWLING GREEN CUSTOM HOUSE

1980 - 1981

INTERIM REPORT

by

Richard Livingston
Office of Research and Development
U.S. Environmental Protection Agency
401 M Street, SW
Washington, D.C. 20460

Marcus Kantz
Jill Dorsheimer
Surveillance and Analysis Division
U.S. Environmental Protection Agency
Region II
Edison, New Jersey

November 20, 1981
Revised March 10, 1983

OFFICE OF EXPLORATORY RESEARCH
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, DC 20460

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA-600/6-84-003		

4. TITLE AND SUBTITLE
Stone Deterioration Studies at the Bowling Green Customs House

5. REPORT DATE
January 1984

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
Richard Livingston, Jill Dorsheimer, and Marcus Kantz

8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Surveillance and Analysis Division
U.S. EPA, Region II
Edison, New Jersey

10. PROGRAM ELEMENT NO.

11. CONTRACT/GRANT NO.

12. SPONSORING AGENCY NAME AND ADDRESS
Office of Exploratory Research
Office of Research and Development
U.S. Environmental Protection Agency
Washington, DC 20460

13. TYPE OF REPORT AND PERIOD COVERED

14. SPONSORING AGENCY CODE
EPA/600/20

15. SUPPLEMENTARY NOTES

16. ABSTRACT

As part of an international program investigating the effect of air pollution on stone monuments, a field study was conducted at the Bowling Green Customs House in New York City. The study included monitoring of gaseous and particulate air pollutants, and meteorological variables, around the building. In addition, several alternative methods for monitoring air pollution were tested. Effect of air pollution was studied on limestone, marble and sandstone. Dissolution of marble in rainfall was also investigated. This report provides background and description of the project. Data and analysis will be presented in subsequent reports.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
IRMA; stone; marble: X-ray fluorescence; Acid deposition; Runoff analysis: static monitors; NATO-CCMS.		

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
Available to public		65
	20. SECURITY CLASS *(This page)*	22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

2<

PREFACE

This interim report was initially prepared in November, 1981 for presentation at an international meeting of the NATO/CCMS Pilot Study on the Conservation/Restoration of Monuments. This initial version was circulated with a disclaimer to the effect that it had not been through the EPA peer review process.

Subsequently, the report was in fact submitted for EPA peer review. This version has been revised to incorporate the comments and changes recommended by the peer reviewers. Major changes include the addition of more detailed descriptions of monitoring techniques and the citation of pertinent references that became available after the date of the initial version. Some of the illustrations were revised to improve their legibility. Deleted were sections that discussed preliminary results and gave an evaluation of IRMA. This deleted material will be published separately.

ACKNOWLEDGMENTS

The authors of this report wish to express their gratitude to Dr. Norbert Baer and Gertrude Helms of the Conservation Center of the Institute of Fine Arts at New York University for their many valuable suggestions and observations during the course of the program. Fred Haynie of EPA's Environmental Science Research Laboratory in North Carolina also lent his expertise to the design of the program. Dr. Joseph Spatola of EPA Region II played a critical role as the initial leader of the team from EPA's Surveillance and Analysis team at Edison, N.J. Other members of the Edison Laboratory who took part in the monitoring program were Paul Brown, Phil Cornejo, Jennifer Eberle and Trudy Fancher. The cooperation of Barbara Metzger, Director of the Edison Laboratory, and Richard Spear, Chief of the Air Pollution Branch, in making the staff and equipment available for this study is also gratefully acknowledged. The staff of the Environmental Monitoring Systems Laboratory in North Carolina, led by Robert Stevens, provided the x-ray fluorescence analysis of the particulate matter samples. Frances P. Bradow of EPA's Environmental Criteria and Assessment Office provided a very helpful critique of the initial version of this report.

Our thanks also go to the General Services Administration for making available the Custom House site. In particular, Walter Roth, Director of the Historic Preservation staff of GSA, and Roger McNamara and Jack Wolfman of Region II proved to be very helpful.

The National Park Service provided help in several ways. Hugh Miller, Chief Historical Architect of the Park Service, provided many useful suggestions, as well as funds to purchase some of the monitoring equipment. Blaine Cliver of the Boston Regional Office made available the services of one of his staff, Frank Matero, who assisted the Edison team. Subsequently, after the restoration work began at the Custom House, the Park Service provided a new site for IRMA, at Federal Hall on Wall Street, where they were operated by John Robbins.

A special acknowledgement goes to Lee Kimche, former Director of the Institute for Museum Services, for her help in completing the interagency arrangements for the program at the Custom House. Finally, the interest and encouragement of Senator and Mrs. Daniel P. Moynihan in the CCMS Program in general and the Custom House activity in particular is deeply appreciated.

TABLE OF CONTENTS

Page

I. Introduction....1
- A. Purpose of Interim Report....1
- B. CCMS Pilot Study on the Conservation/ Restoration of Mouments....1
- C. Objectives of the Custom House Program....2

II. Experimental Approach....4
- A. Background....4
- B. Evaluation of IRMA....6
- C. Comparison of In Situ Readings with Regular Monitoring Data....6
- D. Alternate Techniques for Measuring Pollutants....8
- E. Spatial Distribution of Pollution....9
- F. Effect of Acidic Rain on Marble....9

III. Description of Equipment and Narrative of Operations....10
- A. IRMA....10
- B. Passive Monitors....10
- C. Hi-Volume Particulate Samplers....14
- D. Low Volume Particulate Sampler....15
- E. Meteorological Instruments....15
- F. Runoff Experiments....15
- G. Continuous SO_2 and NO_x Analyzers....17

IV. Conclusions and Recommendations....19
- A. Achievement of Objectives....19
- B. Other Recommendations....21

V. References....23

Appendix A. Description of Bowling Green Custom House
Appendix B. German Proposal for IRMA Program
Appendix C. VDI Specifications for IRMA
Appendix D. Notes on the Statue of Phoenicia
Appendix E. Specifications for Precipitation Analysis

FIGURES

1. North Elevation of Bowling Green Custom House.....3
2. Map of Lower Manhattan.....5
3. Location of New York Monitoring Stations.....7
4. Schematic Diagram of IRMA.....11
5. Roof Plan with Instrument Layout.....12
6. Schedule of Monitoring Operations.....13
7. Statue of Phoenicia.....16

I. Introduction

A. Purpose of Interim Report

This document is a preliminary report on the studies conducted at the Bowling Green Customs House(BGCH) in New York City to investigate the impact of air pollution on building materials. Although the data from the BGCH program have not been completely analyzed, this report has been prepared now to provide a summary of the experience of designing and operating such a study. This information is useful in planning the materials effects research program of the Interagency Task Force on Acid Precipitation(IATFAP, 1982). Also, in view of the considerable time that will be required to complete the data analysis, it is desirable to have available a description of the operations and the status of the raw data as of the end of the monitoring activities at BGCH. Each component of the data analysis, when completed, will be submitted for peer review and publication in an appropriate scientific journal.

B. CCMS Pilot Study on the Conservation/Restoration of Monuments

The Customs House research program arose from U.S. participation in the Committee on the Challenges of Modern Society, an international group organized under NATO. In 1979, CCMS agreed to conduct a study on the problems of protecting stone buildings and monuments from the effects of air pollution and other environmental factors. This project, entitled the "Conservation/Restoration of Monuments", took the form of a Pilot Study, in which interested countries pool their resources under the leadership of a pilot country, in this case Greece(Baer et al., 1982). Since a Pilot Study receives no funding from NATO, the participating countries themselves must support the activities.

At the first meeting of the Pilot Study in Athens, October 1979, it was agreed to undertake three major subprojects: compilation of a census of buildings previously treated to protect against deterioration; development of procedures for testing the effectiveness of treatment methods; and third, characterization of environmental factors that are suspected of exerting the greatest influence on stone decay. The Bowling Green Customs House program constituted the major part of the U.S. involvement in this third subproject.

Concurrent with these international developments, an interagency committee was set up in the United States to coordinate U.S. participation. The committee, initially under the chairmanship of the Director of the Institute of Museum Services, included the Smithsonian Institution, the Environmental Protection Agency (EPA), the National Park Service (NPS), the Heritage Conservation and Recreation Service

(HCRS)*, and the General Services Administration.

Part of the U.S. effort under the third subproject concerned the special problems of monitoring at the site of a historic building. GSA volunteered the use of one of its historic properties, the Bowling Green Customs House in New York City; NPS provided technical consultants and funds to purchase certain items of monitoring equipment; EPA provided staff and the bulk of the monitoring equipment, as well as giving overall coordination at the site.

C. Objectives of the Customs House Program

The Bowling Green Customs House(BGCH) is a major historical and architectural landmark(Figure 1), as well as an excellent site for investigating materials problems related to air pollution. Appendix A gives a description of BGCH. The initial objective of the CCMS activity at this site was to evaluate the performance of a specialized air pollution device, IRMA (Immission† Rate Measuring Apparatus) against that of standard techniques for measuring air pollution. IRMA was proposed by Dr. Siegbart Luckat of Zollern Institute, W. Germany, as a simple and inexpensive device for measuring the ambient levels of sulfates, nitrates, chlorides, and fluorides in air around buildings (see IRMA specifications, Appendix C). The IRMA program undertaken by CCMS set up a network of stations around Europe and in the United States. All the 25 units were to be operated simultaneously for a period of a year (later extended to a two-year period) beginning in September, 1980. The program is described in Appendix B. The United States received two units which were installed at BGCH.

Subsequently several other objectives were identified that could be pursued concurrently using the BGCH site. Ultimately, five major objectives were included:

1. Evaluate IRMA's performance.
2. Compare the air pollution readings in situ against measurements at nearby permanent monitoring sites.
3. Assess alternative techniques for measuring various air pollutants.
4. Describe spatial distribution of air pollution levels around the building.
5. Investigate the effect of acidic deposition on marble.

The approach for investigating each of these objectives is described in the next section.

---

*In July 1981, HCRS was abolished and its functions merged with the National Park Service.

†Immission is a German neologism for uptake of air pollution by a receptor, and is the converse of the process of emission of pollutants by a source.

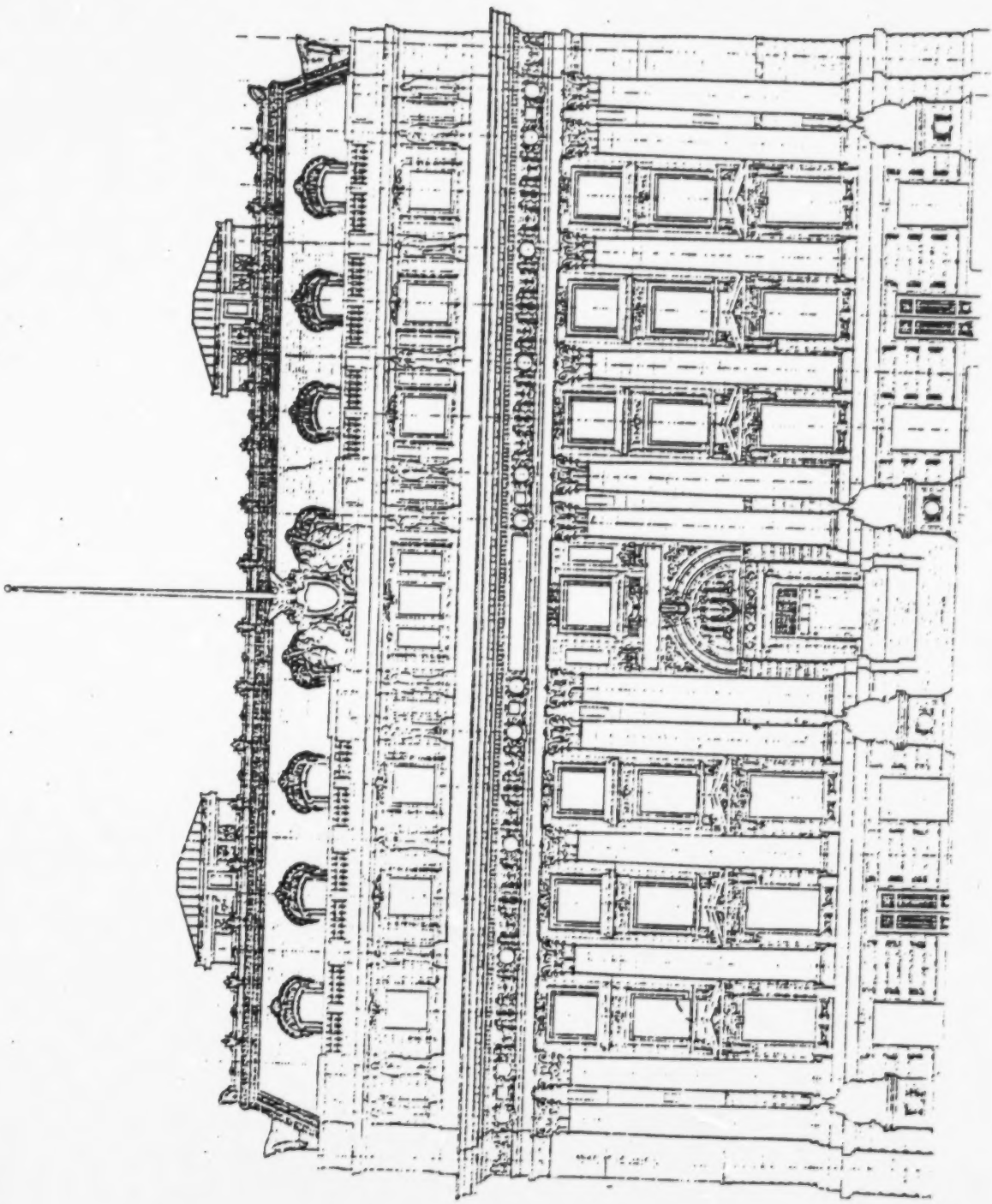


FIGURE 1: BOWLING GREEN CUSTOM HOUSE, FRONT ELEVATION

II. Experimental Approach

A. Background

During this century, it has become evident that air pollution must be considered a major factor in building deterioration, taking its place alongside natural agents of decay such as salt, wind, groundwater, and frost(Torraca, 1981). Relatively little is known about the mechanisms of air pollution attack(Livingston & Baer, 1983) yet this knowledge is required to plan a strategy to minimize stone decay. Issues that need to be resolved include:

- Which are the major pollutants that cause damage?
- What is the characteristic mechanism of damage for each pollutant?
- How to differentiate pollutant effects from those due to natural factors of weathering?
- What techniques are appropriate for measurement of these pollutants in the context of stone deterioration?
- What techniques are suitable for quantifying the damage?

Regarding the first question, the pollutants most often identified as the major cause of decay are various chemical species of sulfur, in the gaseous form of sulfur dioxide, as ammonium sulfates in the form of solid particulates, or as sulfuric acid in rain or snow. This hypothesis is based on the observation of calcium sulfate crusts on limestone, sandstone, or marble surfaces(Fassina et al., 1976). The calcium sulfate arises from the reaction of the calcium carbonate in such stone with the various sulfur species in the environment. This mechanism has in fact been identified as a major mode of deterioration for such monuments as the Erechtheion on the Acropolis of Athens(Skoulikides et al., 1976). However, there are other pollutants such as the nitrogen oxides, that may also cause attack, but which have more soluble reaction products that are washed away by rainfall. Their role in stone decay would thus be harder to identify.

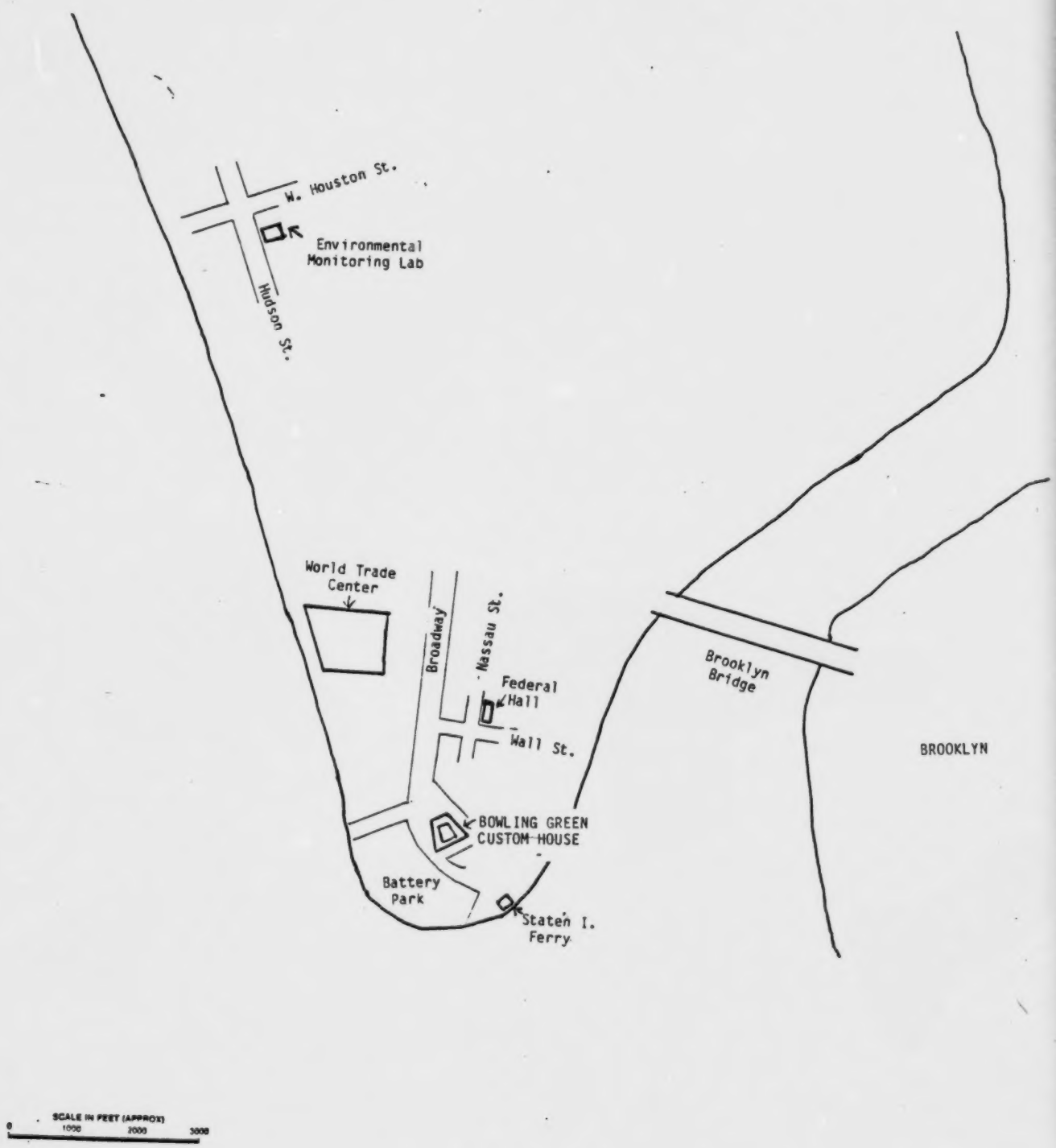
An accurate picture of the major causes of deterioration and the rates of attack at a given site are essential to planning an effective solution to the problem. One option is to reduce the pollution at the source, but this is complicated by the fact that major emitters of sulfur species, such as power plants, may not be the same as those responsible for the nitrogen oxides, such as vehicles. Other options involving the conservation of the stone itself such as treatment or removal are drastic steps and should be considered only if the rate of deterioration threatens the existence of the stone. However, in some situations the observed deterioration is due to higher levels of pollution that occurred in the past, and it must be determined whether significant further damage is taking place at current ambient levels.

Therefore, this project concentrated on the issues of pollution and to a lesser extent, measurement of damage.

---

* For the purpose of this report, the term "stone" is limited to carbonate rocks such as limestone, marble or calcareous sandstone.

FIGURE 2: MAP OF LOWER MANHATTAN



B. Evaluation of IRMA

As noted in the Introduction, the starting point for the BGCH project was the IRMA instrument. However, this technique differs in several basic ways from the techniques recognized by EPA. First, it measures several pollutants simultaneously while EPA reference methods are specific for single pollutants. In IRMA, a film of sodium hydroxide solution is exposed directly to the atmosphere and can react with or absorb a wide variety of pollutants. For example, the amount of sulfate measured in the IRMA solution is a function of both gaseous SO_2 and particulate sulfate in the atmosphere. In effect, IRMA is intended to measure the rate at which sulfate is deposited on a surface--the uptake or immission rate--where the EPA Reference methods are specifically for measurement of ambient concentrations.

Moreover, the IRMA measurements are cumulative over a time period of two weeks, while the techniques approved by EPA are on a time span of 24 hours or less. The instruments most most frequently used by Federal and state air pollution agencies take readings continuously, giving essentially instantaneous measurements.

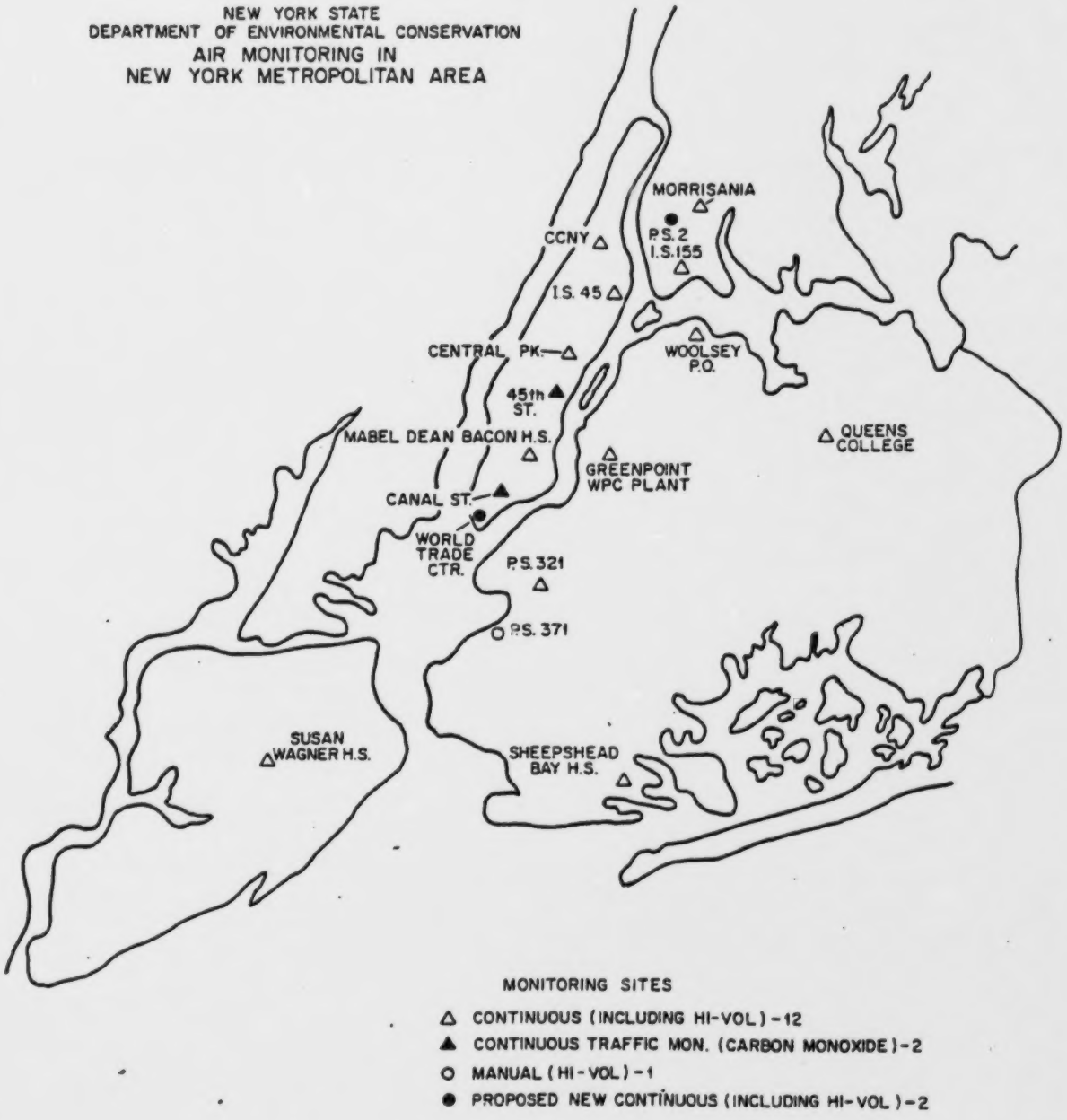
Given these differences, it would not be possible to evaluate IRMA's performance in terms of the specifications set forth by EPA for standard measurement techniques. Nonetheless, the uptake rate measured by IRMA is related to ambient levels. To investiqate this functional relationship the IRMA were co-located with a suite of standard air pollution monitors at BGCH. The instantaneous measurements from the monitors would then be integrated over the IRMA time cycle (14 days) for correlation with the IRMA readings. Since the uptake rate is affected by weather conditions, meteorological data must also be recorded on site.Thus a weather station was installed at BGCH to record wind speed, direction and temperature. Finally, the precision of IRMA would be assessed by installing two units side by side to establish how well the readings tracked each other.

C. Comparison of In Situ Readings with Regular Monitoring Data

Given the presence of the standard air pollution monitors on site, it would be possible to investigate how the readings at BGCH compared to the data from the permanent New York area stations of the national air quality monitoring network (Fig. 3). This would give some insight on the utility of this network for estimating air pollution at a given site for the purpose of assessing building deterioration.

The national network, consisting of more than 250 stations located around the country, is operated by the federal and state environmental protection agencies(CFR,1980). The information from these stations is entered into the STAROAD computer data base maintained by EPA at Research Triangle Park, North Carolina. If the STAROAD data could be extrapolated to any building under study for stone deterioration, it would avoid the considerable effort involved to install equippment at each site to gather the data on local conditions.

FIGURE 3: LOCATION OF NEW YORK MONITORING STATIONS



D. Alternate Techniques for Measuring Pollutants

1. Sulfur Oxides and Nitrogen Oxides- The instrumentation at BGCH also provided an opportunity to evaluate alternate monitoring techniques. The techniques specified by EPA for the national air quality monitoring system for measuring SO_2 and NO_2 use electronic instruments that measure the ambient concentrations continuously and automatically(EPA, 1977). These instruments represent the state of the art, but are expensive and require skilled personnel to keep them calibrated and operating properly. Moreover, they generate large amounts of raw data which must then be reduced to usable form. It is possible that much of this raw data may even be superfluous for studying stone deterioration, which is measured in terms of months or years. In the process of integrating and averaging the instantaneous data over the periods suitable for this purpose, much of the fine detail measured by the continuous analyzers would be smoothed over. Consequently, one of the major needs for specialists involved in the protection of building materials would be the development of cheaper and simpler techniques for measuring SO_2 and NO_x such as IRMA.

Therefore, the program at BGCH also included the testing of two kinds of passive monitors. These consist of petri dishes lined with either lead peroxide in a gel or a filter paper impregnated with potassium carbonate. The plates are mounted so that the active chemicals in the plates are exposed and can react with air pollutants. After a fixed period of exposure, typically a month, the plates are collected and analyzed in the laboratory for accumulated sulfates. In addition the potassium carbonate plates are also analyzed for nitrate and chloride content.

2. Particulate Matter Monitoring- The particulate matter suspended in the atmosphere can affect building materials in a number of ways. For instance, the black crust seen on many older buildings is an accumulation of carbon particles in diverse organic and inorganic forms together with iron oxides and various other constituents (Del Monte et al., 1981). Moreover, certain elements or compounds found in trace quantities in particulate matter such as vanadium may serve as catalysts to accelerate the reactions involved in stone decay(Skiotis et al., 1982). It is also possible that the sulfates contained in the particulate matter may play a major role in the rate of conversion of calcium carbonate to calcium sulfate. Finally, the increased dust loading in the atmosphere contributed by the large particulates will increase the rate of stone abrasion by wind.

The EPA reference method for particulates is the measurement of the mass of total suspended particulates(TSP) in the atmosphere by means of a high volume sampler(EPA, 1977). However, this does not provide any information on the size distribution or chemical composition of the particulate matter. Another technique involves the use of X-ray fluorescence to analyze the elemental composition of particles of a given size range. This requires a different form of sampler.

Therefore, samplers of both types were installed at BGCH for evaluation in the study of stone deterioration.

E. Spatial Distribution of Pollution

Levels of various air pollutants that might affect stone decay are not uniformly distributed about buildings or other structures because of microclimate, wind variations, the pattern of sources and the atmospheric chemistry of the pollutant in question(Benarie, 1981). From general considerations, it is not expected that sulfur oxides would show much variation on this scale(100 meters) in an urban environment like Manhattan where no single source is dominant. It is more likely that NO_x concentrations would vary, because these gases are emitted mainly in vehicle exhaust and react very rapidly in the atmosphere. Thus, NO_x concentrations could be different at different points around the building, reflecting different traffic patterns, and to decrease with increasing elevation.

The approach for studying this spatial distribution of pollutant concentrations consisted of deploying more than one monitor around the building for each kind of pollutant in question. By taking simultaneous readings at different points, a rough distribution pattern could be obtained.

F. Effect of Acidic Rain on Marble

Several major questions concern the actual mechanisms by which precipitation attacks and subsequently removes the stone surface. One is the role played in the stone deterioration process by sulfuric acid in acid rain versus other sources of sulfates such as dry deposition by particulates. Another is how much of the stone erosion comes from the reactions with nitrates in the rain. The nitrate reactions are more difficult to study because the reaction products are much more soluble and thus more readily removed from the system by rainwater runoff.

These questions were investigated through solute studies of rainwater runoff. Specifically, a series of experiments were planned to be conducted during rain events to collect rainwater runoff from one of the marble statues and the concentrations of major ions in the water analyzed. At the same time, the incident rain was also collected and its ionic composition analyzed for comparison. The changes in ionic concentration would be an indication of the reactions taking place.

III. Description of Equipment and Narrative of Operations

A. IRMA

The two units of the Immission Rate Monitoring Apparatus (IRMA) utilized at the BGCH were supplied by the Federal Republic of Germany and served as the focus of the BGCH project. The IRMA's central element consists of a thimble-shaped paper filter which is continuously washed by a sodium hydroxide solution(see Fig. 4). Air pollutants come in contact with the layer of fluid on the thimble's external suface and and are taken up by the solution. The unit is installed on a special stand that shields it from precipitation. The solution and filter are changed every two weeks and returned to Germany for analysis of absorbed sulfates, nitrates, chlorides and flourides. For a more detailed description of IRMA, see Appendix C.

In addition to the IRMA instrument itself, the full installation includes two revolving carousels on which stone samples are mounted. The stones provided were German Baumberg sandstone and musselkalk(fossiliferous limestone). These particular stones have proven to be very sensitive to air pollution. Six plates of each stone are mounted on each carousel. After the two year exposure period, the plates were removed and returned to the Zollern Institute for analysis by weight loss and wet chemistry.

The two IRMA were installed and operated on the roof on the west wing of the BGCH(see fig. 5). The thimbles and solution bottles were changed every fourteen days commencing on 9/15/80 to coincide with the schedule agreed upon by the CCMS participants. In addition, the batteries were changed every cycle and the peristaltic pumpheads changed every other cycle or as needed. The used pumpheads were then returned to Germany for repair and reconditioning, or reconditioned by EPA staff at the Edison Laboratory.

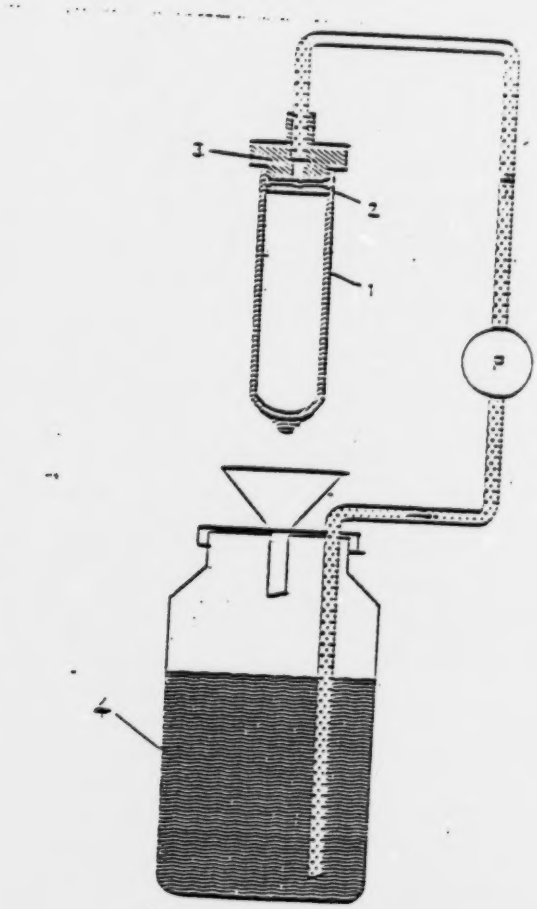
On October 29,1980 one of the IRMAs(unit #20) was blown over in a heavy wind storm. The stand was discovered tilted 30° from vertical. The unit itself was undamaged but several stone coupons were broken. On several occasions one or both of the units ran out of solution before the end of the sampling cycle. Batches of samples were sent to the Zollern Institute on 12/19/80, 3/1/81, 5/26/81 and 8/7/81. These batches cover sampling cycles 1 through 20. As of the date of this report, no results of the analysis have been received from Germany.

On July 15,1981 the two units were relocated to the roof of Federal Hall at 26 Wall St. This move was necessitated by the commencement of restoration at the BGCH. Federal Hall, a National Historical Monument maintained by the National Park Service, was selected because of its proximity to BGCH and because Park Service personnel were available continuously on site to operate the equipment. The operations are summarized in figure 6.

B. Passive Monitors

Sulfation plates manufactured by Research Appliance Co. were installed at several locations around the building. The plates consist of plastic petri dishes coated with a layer of lead peroxide particles

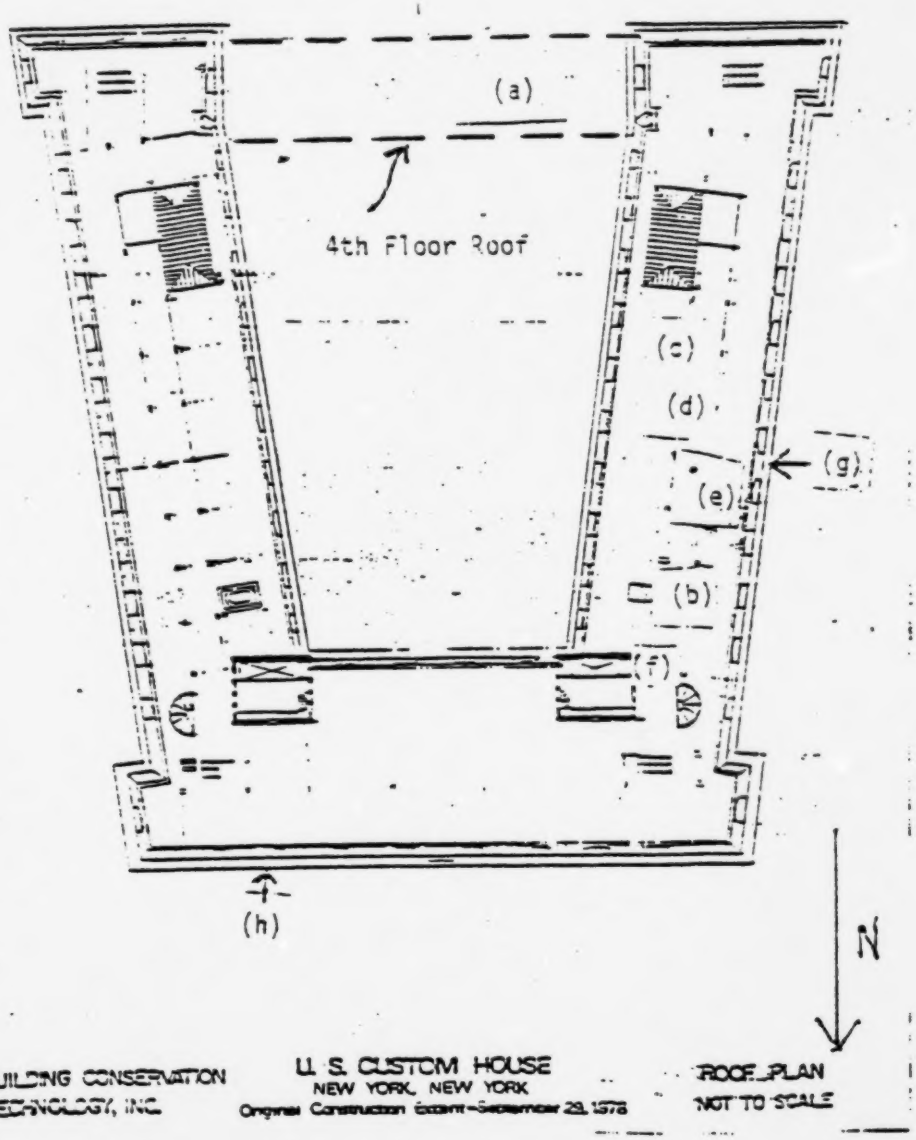
FIGURE 4: SCHEMATIC DIAGRAM OF IRMA



1. Filter Paper Thimble
2. Solution Distribution Passages
3. Thimble Holder
4. Solution Reservoir

P. Peristaltic Pump

FIGURE 5: ROOF PLAN WITH INSTRUMENT LAYOUT

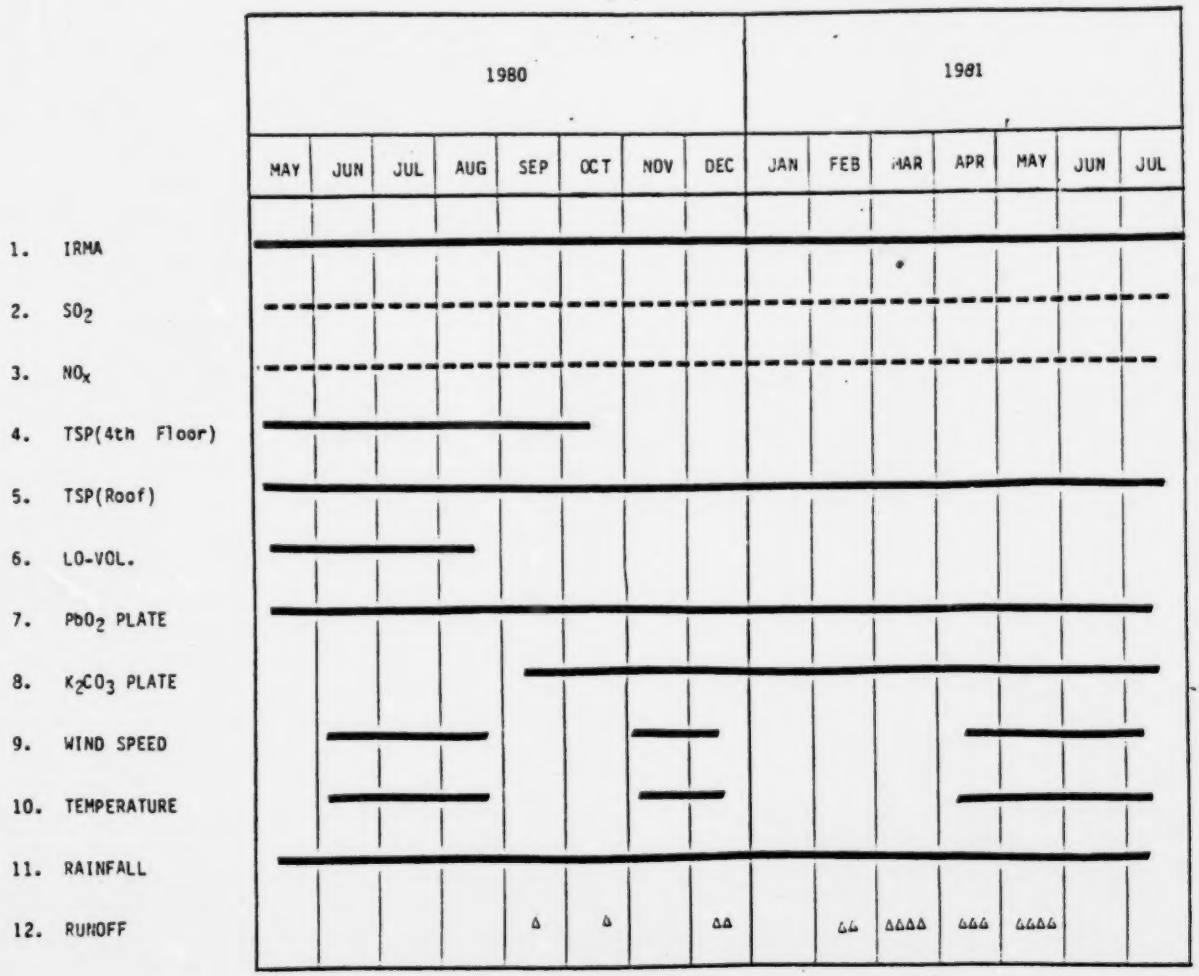


KEY

(a) Hi-vol, 4th Floor Roof
(b) " Main Roof
(c) IRMA Unit 19
(d) " " 20
(e) Meteorological Tower
(f) Low-volume Sampler
(g) Probes for SO_2 and NO_x Analysers, (2nd Floor window)
(h) Statue of Phoenicia(6th Floor)

Reproduced from best available copy.

FIGURE 6: SCHEDULE OF MONITORING OPERATIONS



in a gum tragacanth binder(APHA,1977). The plates are installed with the active surface oriented downward to avoid being wetted by rain.

Acid gas(or carbonic) plates are similar in principal to lead peroxide plates except that the active element is a filter paper wetted with a potassium carbonate solution. The filter paper is then mounted in an open Petri dish. The acid gas plates were supplied by Serco Co. of Cedar Falls, IA. These plates are installed in the same fashion as the sulfation plates to avoid wet deposition.

The first set of lead peroxide plates were installed on May 2, 1980. Each set was exposed for approximately thirty days. The main series of plates was located at the roof level on each IRMA stand, and on the statue of Phoenicia at the sixth-floor level. Sampling at these locations was maintained continuously from May, 1980 until July, 1981, except for the period of August 1 to September 15, 1980. During the months of June and July, 1980, a supplemental series of plates was installed at the second and fourth floor levels. The series of acid gas plates began in October of 1980 and ran through the termination of operations. The operations are summarized in **figure 6.**

The lead peroxide plates were analyzed for sulfate only by Princeton Aqua Sciences using the standard turbidimetric method(ASTM-D-517). The acid gas plates were analyzed by Serco using turbidimetric methods for sulfate, colorimetry(ASTM-D-992) for nitrates, and titration(ASTM-D-1253) for chlorides. All plates have now been analyzed.

C. Hi-Volume Particulate Samplers

Two hi-volume particulate samplers, or "hi-vols," were employed at the BGCH to measure the mass of total suspended particulates(TSP). A hi-vol is the standard ambient air particulate matter measurement apparatus, which draws the air through a glass fiber filter which collects the particles. For a detailed description of the equipment see EPA, (1977). Hi-vols are normally set to run for 24 continuous hours once every 6 day. By weighing the filter before and after collection, the total mass of particles on the filter is determined. From this, the concentration of particulate matter suspended in the air can be estimated.

One of the hi-vols was put in place on the fourth floor level; the other was located on the seventh floor roof with the IRMA and the meteorological equipment(see fig. 4). Initially the hi-vols were operated on a three-day cycle beginning May 3, 1980. No data were collected during the period from July 17 to September 1, 1980. After that date, the standard six-day cycle, synchronized with the national monitoring network, was adopted. At the same time it was decided to discontinue the measurements on the fourth floor level due to persistent anomalously high readings, presumably caused by resuspended roof dust. The seventh floor monitor continued in operation until July 1, 1981. **The operations are summarized in figure 6.**

Each filter sample was weighed before and after exposure. The weighing was performed at Edison Laboratory using a torsion balance, Christian Becker model EA-1-AP.

D. Low Volume Particulate Sampler

A low-volume particulate sampler was utilized at BGCH to collect fine particulate matter(<10 um in diameter) in order to assess the elemental distribution in the suspended particulate matter. It consisted of a size-selective inlet, a fine-pore teflon filter, and 2 liter/min. pump to draw the air through the filter. After exposure the filter samples were analyzed by X-ray fluorescence for the elemental distribution at EPA's Environmental Science Research Laboratory in North Carolina.

The low volume particulate sampler was installed on the roof of BGCH adjacent to the hi-vol(Fig. 4). The sampler was run for 24 hours every third day, beginning on May 10, 1980. This continued through August 19, 1980, when the inlet system broke down. A total of 31 samples were collected and all have been analyzed. See figure 6 for summary.

E. Meteorological Instruments

Standard meteorological data were also collected during the BGCH project. All meteorological equipment was located on the seventh floor roof. A wind monitor continuously measured wind speed and direction, which were recorded mechanically on strip charts. Temperature data were similarly recorded. A manual rain gauge was used to record the cumulative amount of rain that fell on the roof between visits. The rainfall gauge reading was recorded at least every two weeks.

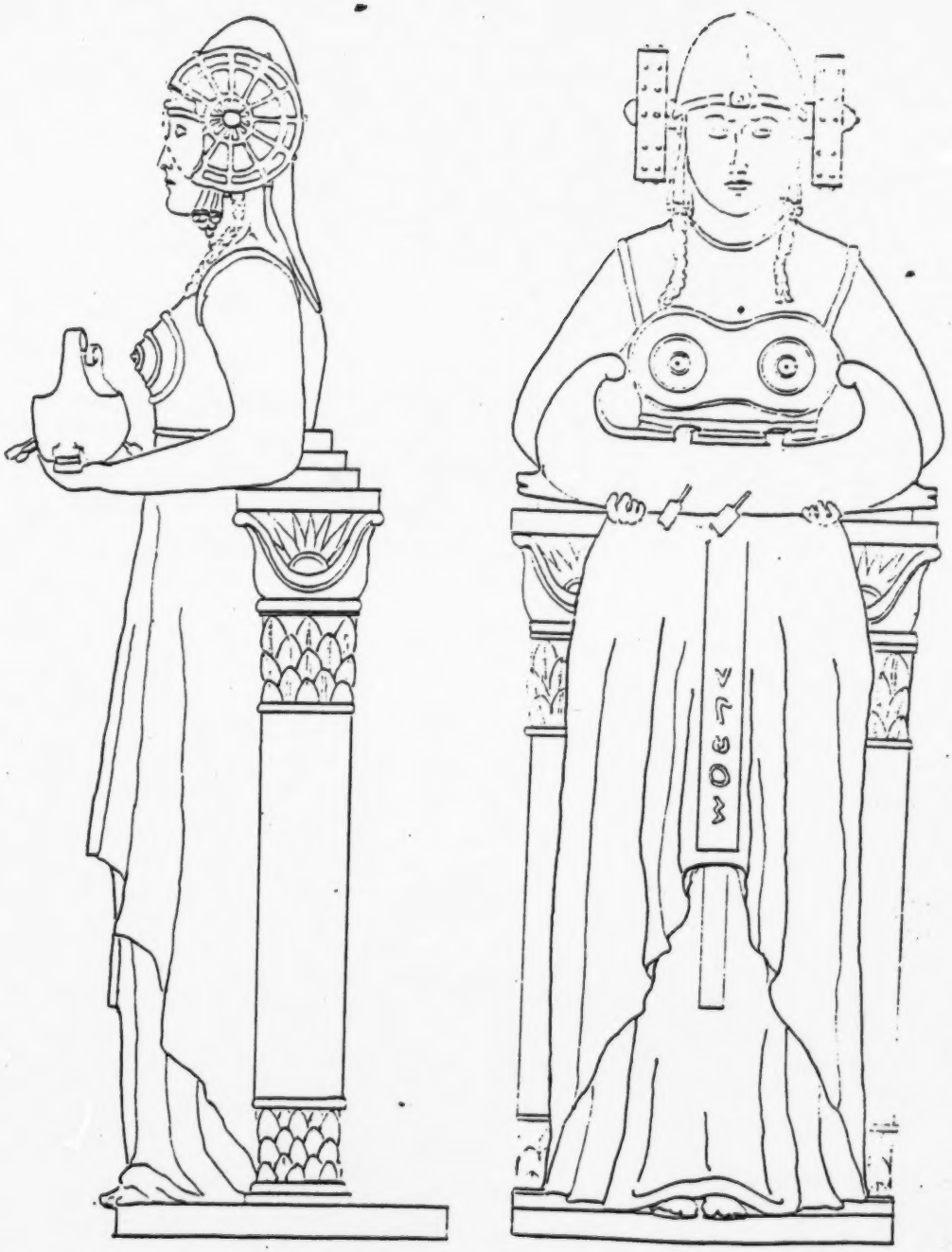
The meteorological monitoring began on June 27, 1980 and continued until September 19, 1980 when the anemometer was damaged and required repair. Operations resumed on October 20 and proceeded until December 10 when the mechanical recording system broke down. The instruments were inactive until April 16, 1981. Data collection resumed on that date and continued uninterrupted until the termination of operations at BGCH on July 1, 1981. Therefore, meteorological data in strip chart form are available for approximately seven months out of the entire study period(Fig. 6). The strip chart data have not yet been completely tabulated.

F. Runoff Experiments

The investigation of the effect of acidic precipitation on building materials focused on the marble statue of Phoenicia located on the sixth-floor level of the North facade. The statue(Fig. 7) is nine feet tall and stands on a 40" by 40" base. Appendix D gives more details. The approach was to develop mass balances of the principal ions involved in the process of stone decay, e.g. calcium, sulfate, and nitrate. This was done by comparing the material washed off the statue during a rain event with the incident rainwater.

The procedure called for collecting simultaneous samples of water of incident rain and of the resulting runoff from the statue. The samples would then be analyzed for concentrations of the specified ions: sulfate, nitrate, ammonia, chlorine, sodium, magnesium, potassium and phosphate(see Appendix E). Also measured in each pair of samples were

FIGURE 7: STATUE OF PHOENICIA



pH and conductivity. In addition, a series of washdowns with distilled water were conducted as a control. The runoff from the distilled water was collected and analyzed in the same way as the rainwater runoff.

The runoff collection apparatus consisted of polyethylene guttering fixed around the perimeter of the base of the statue. Polyethylene tubing led the runoff by gravity from the gutters to 17 liter containers placed at the base of the pedestal. Leakage was avoided by the use of inert caulking and teflon paper barriers.

The incident rainfall was collected in 5 gallon glass containers fitted with large plastic funnels. These containers remained permanently open and served as passive samplers, collecting all the rainfall that fell over the duration of the sampling cycle. This method of sampling, known as bulk collection, also collects particulate matter during dry periods, in contrast to the dual-bucket apparatus that samples wet deposition and dry deposition separately(Galloway and Likens, 1976). The resulting pH and ionic concentrations from the bulk collector are thus not directly comparable to that of the dual-bucket collector. After each sample was collected for analysis, the containers and funnels were rinsed with distilled water and put back in position. It was found necessary to put out several of these collectors in order to acquire enough sample from a given rain event to provide adequate water(about 2 liters) to carry out all the specified analyses.

Although it is preferable to collect the samples immediately after each individual rain event, this was usually not possible given the other demands on the staff's time. In a few cases, precipitation samples were picked up immediately after a rainstorm, but generally the samples were taken during the regularly scheduled visits and thus combined several different rain events. A total of 23 runoff samples were collected, in addition to 15 washdowns with distilled water. However, due to lack of sufficient volume of rainfall samples for the earlier events, only the 8 most recent cases could be fully analyzed. These were taken in the months of March through May of 1981(figure 6).

The analyses were performed by Edison Laboratory staff. The cations were determined using atomic absorption spectrometry on a Beckman 5000 instrument. The anions were measured by colorimetry on a Technicon Autoanalyser II. Conductivity was measured with a Leeds & Northrup conductance meter, and the pH was measured electronically on a Beckman 3550 pH meter. These techniques are described in detail in Methods for Chemical Analysis of Water and Wastes(EPA, 1974).

G. Continuous SO_2 and NO_x Analyzers

In order to make precise and continuous determinations of ambient concentrations of SO_2 and NO_x, electronic analyzers were utilized. Two different makes of SO_2 monitors were used: a Beckman model 953 and a Teco. The NO_x was measured by a Monitor Lab 9440E unit. The instruments and associated strip chart recorders were located indoors in a room on the second floor of the west wing (Fig. 4). Probes for the analyzers were led out the room window to the exterior of the building.

The equipment was installed and began operating on May 13, 1980. However, because the building heating plant had been shut down, a stable thermal environment could not be provided. This caused the data to be unreliable. A temperature-controlled shelter was ordered, but due to delays in shipment it did not arrive in time to be used. Therefore, the data from the analyzers should not be considered usable.

IV. Conclusions and Recommendations

At this time, it is still too early to predict how much will be accomplished toward each objective although enough data have been collected so that all five can be satisfied to some degree. The in situ work at Bowling Green Customs House has been terminated and the chemical analyses completed with the notable exception of the IRMA data. The majority of the data reduction and statistical analysis remains to be done. It is already known that because of the inability to collect some of the data as originally planned, certain objectives will only be partially accomplished. However, significant results will still be obtained.

This section summarizes the present stage of progress for each objective and recommendations for future activities. Also included are some more general recommendations for such research.

A. Evaluation of IRMA.

The absence of reliable SO_2 and NO_x data measured on site is a major setback to evaluating IRMA's performance. Fortunately, other measurements made during this experiment will permit the assessment of several several aspects of IRMA's performance, once the data are supplied by the Zollern Institute. This could include:

1. Measurement of sulfate uptake by IRMA vs. sulfation plates.
2. Comparison of SO_x data from IRMA vs. nearby permanent monitoring stations.
3. IRMA vs. particulate collectors for measuring chlorides.
4. Effect of meteorological variables on IRMA's performance.
5. Precision of IRMA measurements by comparison between the two units.

Recommendation- The complete evaluation of IRMA would still require side-by-side sampling with standard monitoring equipment for at least one full annual cycle. Furthermore, spatial or temporal variations of air pollutants or micrometeorology that would complicate the assessment of the data should be minimized. This is best done by choosing a site that is relatively simple to characterize in terms of air pollution sources and local climate, although this may conflict with the stated goal of the NATO/CCMS Pilot Study to operate IRMA at a historic site.

B. Comparison of In Situ Monitoring with Regular Data.

This objective can be only partially accomplished because of the lack of reliable data from the continuous SO_2 and NO_x monitors. However some comparisons can still be made using the results from the lead peroxide and acid gas plates. In addition, the rainfall analysis can be compared with the data from the nearest wet deposition collection station. In this case, one operated by the Department of Energy(DOE) at 376 Hudson St.(see figure 2). The TSP and x-ray flourescence data on particulates can also be compared with the results from the DOE station as well as the NY State air pollution monitoring network. Finnally, meteorological data collected at BGCH can be compared with that from the stations in the vicinity operated by various agencies.

However, based on the preliminary results of the spatial variation studies at BGCH, we feel that it has been sufficiently demonstrated that on-site monitoring is usually required for gaseous pollutants.

Recommendation- Before conducting further field investigations for this objective, modeling studies should be conducted to determine the variations that might be expected for a given terrain and spacing between site and monitors.

C. Alternate Techniques for Measuring Pollutants.

Again this objective cannot be fully accomplished due to the lack of continuous SO_2 and NO_2 data on site. It should still be possible to compare the performance of the three SO_2 measuring techniques that were tried --IRMA, lead peroxide, and acid gas plates-- against each other, and against the data from nearly permanent stations. Sufficient data have been collected to accomplish the assessment of the two particulate collection techniques tested -- the high-volume sampler and the low-volume teflon filter technique-- for monitoring both seasonal TSP variations and trace element distributions.

The utility of passive monitor techniques for detecting air pollution at building sites has been demonstrated, especially as backup to active monitoring methods. Although detailed comparisons between the methods remain to be done, these techniques are especially promising because they are inexpensive, low in labor requirements, and yield sulfate deposition rates directly. The x-ray fluorescence method and complementary techniques such as quantitative x-ray diffraction and neutron activation analysis are worth studying because of the need to investigate trace materials that may affect stone deterioration in various ways. Also desirable is the characterization of the physical form(fly ash, marine aerosol, etc.) of the particles.

Recommendation- The assessment of the utility of these monitoring techniques should be continued in any further research. The particulate research should be extended to cover sodium,fluorine and carbon, both organic or inorganic. Analytical techniques for particle morphology should also be investigated.

D. Spatial Distribution of Pollutants.

This objective was only partially accomplished because there was not enough time to carry out a series of simultaneous SO_2 and NO_x measurements at different points on the building. The TSP was measured at two different locations on the building, but the measurements on the fourth floor roof are seriously suspect because of resuspended dust from the roof.

Detailed study of the spatial variation of pollution around the volume of a building can certainly produce interesting information, and could prove to be of some value for the preservation of a specific building. However, such study would be very elaborate since it would require weather measurements, including three-dimensional resolution of wind direction, at several points around the building simultaneously. Air pollution intruments would also have to be installed at each point. Such a monitoring program would be on a much larger scale than originally envisioned for the CCMS Pilot Study.

Moreover, to be most effective the study of spatial distribution around the exterior of the building should be supplemented by monitoring of interior pollutant levels and building structural response. This would best be undertaken a separate project.

Recommendation- Spatial variation studies,despite their value, should not be pursued as part of the present CCMS Pilot Study unless the resources available are significantly increased.

E. Acidic Deposition on Stone

An initial set of experiments has been carried out, but conclusions are difficult to reach because of the extremely complex interactions and the difficulties in collecting representative data. However, further evaluation of the data should still divulge useful information concerning the degradation processes of stone. It is already evident that further studies will probably have to investigate the processes of acidic deposition and material removal separately.

The BGCH study has clearly shown the problems of studying these processes using materials as found on site. The use of weathered materials like the stone of the statue of Phoenicia at the Customs House introduces a vast array of uncontrolled or unmeasurable variables into the study. These include unknown variations in stone porosity, composition and finish as originally made and subsequently changed with exposure. Questions can also be raised about the presence of a variety of chemical compounds on or in the stone, representing the accumulated products of earlier environmental deposition or attack, as well as catalysts or buffers deposited on the surface. Finally, because of its configuration, the surface of the stone was not uniformly exposed to the elements or to the acid deposition.

In the long run, is imperative to do some work with new stone in a laboratory setting under controlled conditions, simulating pollution and rainfall in carefully measured amounts. However, it is likely that useful field studies could also be performed using specially prepared stone samples exposed in situ with appropriate monitoring equipment. The assessment would include collection of wet and dry deposition and rainwater runoff from the samples.

Recommendation- Some form of materials effects measurement should be included in any future research. However, this should focus on the use of specially prepared samples both in the laboratory and in situ.

F. Other Recommendations

In addition to the recommendations pertaining to specific objectives of of the BGCH study, there are a number of considerations that cover all of the activities of the program. The following are generally applicable:

1. Measurement Cycles- The BGCH operations were conducted on a fixed schedule in order to synchronize with other monitoring installations. However, for materials effects work the most significant time intervals appear to run between

between rain events, which serve to remove significant amounts of surface material accumulated during dry periods. All the variables should preferably be measured on a daily basis, but if this is not possible, then the next best set of cycles would not be a calendar basis, but rather from one rain to the next.

2.Data Manipulation- Considering the large number of data points and the vast number of possible correlations between variables, it would be worthwhile to design a format for systematically recording data. This format should be drawn up to permit manipulation by computer. It would also be extremely desirable to collect the data on digital electronic form whenever possible.

3.Access and Inspection- Certain samples require immediate collection and analysis to yield the most useful data, e.g., rainfall, or sulfate particulates. Also the processes being studied involve measuring a large number of variables simultaneously, so that if one of the instruments fails, the value of the rest of the data for that time interval is considerably impaired. Therefore, constant on-site attendance or at least daily visits to collect samples and to check the operation of the instruments would be highly recommended.

4. Redundancy of Measurements- As much as possible, the critical variables such as SO_2 should be measured in a number of different ways so that the data can still be recovered in the event of the failure of the primary monitoring instrument.

5. Data Averaging- Before undertaking further monitoring activities consideration needs to be given to how the data will be averaged or aggregated for ultimate use. For many environmental variables, a monthly average may be sufficient for materials effects work. Also different averaging techniques may be used for various circumstances. For example, SO_2 is usually reported on a arithmetic average while TSP is reported on a geometric average basis. However, for reporting seasonal variations of SO_2, a root-mean-squared average has also been used. The type of averaging chosen may influence the choice of monitoring equipment or data processing.

6. Site Selection- The BGCH was selected as the site for this study because it represented a historic building in polluted environment. To a certain extent this resulted in a compromise in achieving the various objectives. In future work, it will probably be necessary to use more than one site to carry out the research. One type of site would be used for exposure of material samples and evaluations of monitoring equipment. The other would selected in order to study building-oriented problems such as spatial variation of pollutants and microclimates.

REFERENCES

APHA(American Public Health Association), 1977, Methods of Air Sampling and Analysis, Washington, DC, p. 691.

Baer, N., G. Helms and R. Livingston, 1982, "The Conservation/Restoration of Stone Monuments: A Progress Report on the NATO-CCMS Pilot Study" 4th International Congress on the Deterioration and Preservation of Stone Objects, U. of Louisville, Louisville, Kentucky (in press).

Benarie, M., 1981, Urban Air Pollution Modelling, The MIT Press, Cambridge,MA pg. 151.

CFR(Code of Federal Regulations), 1980 "Ambient Air Surveillance" Title 40, Part 58, U.S. Government Printing Office, Washington, DC, p. 144.

Del Monte, M., C. Sabbioni and O. Vittori, 1981, "Airborne Carbon Particles and Marble Deterioration", Atmospheric Environment, Vol. 15, pp. 645-652.

EPA (US Environmental Protection Agency), 1974, Methods for Chemical Analysis of Water and Wastes, PB 259 973, National Technical Information Service, Springfield, VA. 298 pp.

---------- , 1977, Quality Assurance Handbook for Pollution Measurement Systems, PB 273 518, National Technical Information Service, Springfield, VA, 530 pp.

Galloway, J. and G. Likens, 1976, "Calibration of Collection Procedures for the Determination of Precipitation Chemistry", Water, Air and Soil Pollution, Vol. 6, pp. 241 - 258.

ITFAP(Interagency Task Force on Acid Precipitation), 1982, National Acid Precipitation Assessment Plan, Council on Environmental Quality, Washington, DC 92 pp.

Livingston, R. and N. Baer, 1983, "Mechanisms of Air Pollution-Induced Damage to Stone", VIth World Congress on Air Quality, Paris (in Press).

Skiotis, D., D. Paradelis and V. Katsev, 1982, "Catalytic Oxidation of SO_2 on Marble Surfaces", 3rd International Congress on the Deterioration and Preservation of Stone, Venice

Skoulikides, T., P. Papakonstantinou and D. Charalambous, 1976, "Attaque Atmospherique (marbres) et mesures a prendre", 2nd International Symposium on the Deterioration of Building Stones, ed. N. Beloyannis, Ministry of Culture and Science, Athens, pp. 327 - 342.

Stevens, R., T. Dzubay, G. Russwurm and D. Richel, 1978, "Sampling and Analysis of Atmospheric Sulfates and Related Species", Atmospheric Environment, Vol. 12, pp. 56 - 68.

Torraca, G., 1981, Porous Building Materials-Materials Science for Architectural Conservators, International Centre for the Study of the Preservation and the Restoration of Cultural Property, Rome, pp. 37 - 48.

Appendix A. Description of Bowling Green Custom House

HISTORY OF THE BOWLING GREEN CUSTOM HOUSE

by Richard A. Livingston

The Bowling Green Custom House is a prominent symbol of both the Beaux Art school of architecture and the importance of the New York Customs District. For most of the Custom Service's history since its founding in 1789, this District, which includes the New York Harbor ports of both New York and New Jersey, has supplied the greatest single share of the nation's custom revenue. At the turn of the century, when the Bowling Green Custom House was being planned, this District alone collected more than two-thirds of the total United States duties on imports.[1] This record, together with its location in the heart of Wall St. called for a suitably impressive building.

The historical significance of the Custom House site on the tip of Manhattan dates to the initial Dutch settlement of New Amsterdam in 1626. At that time, Fort Amsterdam was erected on this strategic location, which continued to be used for fortifications until the end of the Revolutionary War. In 1787, the fort was demolished, and in its place was built Government House, which was intended to be the President's official residence. Instead, when the U.S. capital was established in Washington, Government House served initally as the executive mansion for the Governors of New York. Then, from 1800, it was used as the custom house until 1815, when it burned down. The site was then occupied by a collection of shops and businesses[2].

Subsequently, a number of different buildings in the Wall St. vicinity were used for the Custom House, most notably Federal Hall from 1840 to 1863[3]. After Federal Hall, customs activities were moved to the larger Old Merchants' Exchange building, but by the 1890's, it was evident that still more space would be needed[4]. Eventually, in 1899, the US Treasury Department purchased the Bowling Green site at a cost of $2,200,000[5] and announced a design competition for a new building.

The winning design was submitted by Cass Gilbert, who was just beginning a distinguished career. After Bowling Green, he went on to design such landmark buildings as the Woolworth Building, the US Treasury Annex and the Supreme Court Building. Gilbert's design for the Custom House reflected the prevailing Beaux Arts style, which favored the use of classical architectural elements combined with elaborate ornamentation and statuary.

The plan of the Custom House is U-shaped, with the open or south side facing the Harbor. The main entrance is on the North

side fronting on Bowling Green. The building is rectangular in elevation, 128 ft. high by 290 ft. along the sides. The net square footage is 236,600[6].

In the central space defined by the two wings of the sides, Gilbert placed an oval rotunda four stories high. The dome of the rotunda, designed by Guastavino, consists mainly of a skylight[7].

Along each side are twelve unfluted columns. On the east and west sides, the columns are evenly spaced between windows, while on the front, they are paired at the corners and at either side of the entrance. The capital of the column is basically Corinthian, but modified by the addition of a head of Mercury as the god of commerce.

The sculptural ornaments are generally nautical in theme, as can be seen in the scallop shells over the dormer windows and the tridents used as acroteria. Gilbert used to the major statuary to emphasize the rhythm of the facade. The four groups at ground level, representing the four continents, accentuate the four pairs of doubled columns. Each of the twelve statues at the roof level, representing the maritime nations, is placed above one of the columns and thus serves to continue the vertical lines above the cornice. The cartouche at the top marks the entrance but also ties the two halves of the facade together.

Gilbert chose light-colored stone for the statuary in order to highlight these accents against the dark granite of the building exterior. A further refinement lay in the choice of white limestone for the ground level statues and pink marble for contrast on the upper stories. Some of this effect is now lost however, because the pink marble has weathered to a white color.

The sculptor and subject for each of the statues was personally selected by Gilbert. They are listed in Table I. The proess is described in more detail in the Appendix entitled "Notes on the Statue of Phoenicia". The sculptors were all prominent in their day, but Daniel Chester French is perhaps the best known.

The specifications for the construction of the building called for reinforced concrete foundations and steel frame masonry walls with a granite ashlar facing. Copper was extensively used for guttering and decorative window frames.

Gilbert also put much effort into the decoration of the interior. The entrance was finished in a variety of marbles from

TABLE I: STATUARY OF BOWLING GREEN CUSTOM HOUSE[10]

1. Ground Level- The Four Continents

(left to right)

Asia
N. America (All by Daniel Chester French)
Europe
Africa

2. Roof Level - The 12 Maritime Nations

(left to Right)

Greece ..... Frank Elwell
Rome..... " "
Phoenicia..... Frederic W. Ruckstull
Genoa..... Augustus Lukeman
Venice..... F.M.L. Tonetti
Spain..... " "
Holland..... Louis St. Gaudens
Portugal..... " "
Denmark..... Johannes Gelert
Germany..... Albert Jaegers
(or Belgium)
France..... Charles Grafly
England..... " "

3. Roof Level-Cartouche...Karl Bitter

Switzerland, Italy, Georgia, Alaska and Vermont[8]. The waitng room of the Collector of Customs is lined with elaborate wooden panelling and contains ten paintings of seventeenth century sea ports by Elmer Garnsey[9].

Excavations began in 1899. The contractor for the foundations was Isaac Hopper & Son. John Pierce & Company was the contractor for the superstructure and J.C. Robinson and Sons for the interior. Strikes, shortages of materials and various other problems caused the schedule to slip beyond the May 4, 1905 deadline. The Customs Service finally moved into the building on November 7, 1907[11].

Several significant events concerning the building's fabric took place during the period of occupancy. In 1914 and again in 1941, the main entrance was re-designed for revolving doors. In 1937, as a WPA Federal Arts Project, Reginald Marsh painted a series of murals in the rotunda depicting the various stages of a steamship's arrival into port. During World War II, the rotunda skylight was blacked out by a coating of pitch which still remains. In 1938 and in 1976, the building exterior was cleaned[12].

In October, 1965 the New York City Landmarks Commission designated the Custom House as a City landmark[13]. This coincided with an evaluation by the General Services Administration of the future use of the building. At the time, it was felt that because of the relatively low ratio of usable office space in the Custom House, the outlays required for renovation could not be justified[14]. Consequently, the Customs Service moved to new quarters in the World Trade Center in 1973[15].

Several years of debate over the use of the now vacant building then ensued. In 1974, it was awarded status as a National Register Landmark[16]. Finally, in 1978, Federal legislation was passed appropriating $29 million to restore the Custom House to active use as an office building available for both government and private sector occupants[17].

The General Services Adminstration then conducted a design competition for the restoration and conversion of the building. In January, 1980, the winning team was announced. It is a joint venture of Marcel Breuer Associates, James Stewart Polshek and Associates, Stewart Daniel Hoban and Associates, and Goldman-Sokolow-Copland. The restoration design minimizes major changes to the original Cass Gilbert plans[18].

In July,1981 preliminary restoration work began.

REFERENCES

1. Ernest L. Chambre (1973) "Two Centuries of Tradition in one Square Mile", Via Port of New York, Port Authority of New York.

2. Lenard (sic) E. Brown(1967) History of The United States Custom House, 1 Bowling Green, New York, New York, National Park Service, Division of History, Washington DC pg.6.

3. Joseph P. Kelly(no date),"The Custom House, New York",U.S. Custom Service, New York District, p.20.

4. Brendan Gill (1976) The U.S. Custom House on Bowling Green, New York Landmarks Conservancy, Inc., New York, NY, pg. 5.

5. Lenard E. Brown, op. cit., pg. 2.

6. Historic Preservation Staff, GSA (no date)"Inventory of Materials and Construction, U.S. Custom House."Washington, DC.

7. Brendan Gill, op.cit., p. 12

8. Ibid., p. 12.

9. Lenard E. Brown, op. cit. , p. 5

10. Ibid.,p.12

11. Ibid., p.2

12. Historic Preservation Staff, GSA, op. cit.

13. New York Times, October 13, 1965, p.37.

14. Lenard E. Brown, op. cit. p. 9

15. Ernest L. Chambre, op. cit.

16. National Park Service, Register of Historic Places,

17. PL ***

18. Ada Louise Huxtable,(1980),"An Enlightened Plan for Converting the Custom House",N.Y. Times, October 6, 1980, p.25.

Appendix B. German Proposal for IRMA Program

GERMAN PROPOSAL* FOR A MEASURING PRORAMME AS PART OF THE NATO-CCMS STUDY, "CONSERVATION/RESTORATION OF MONUMENTS"

III. Assignment of Tasks and Approach to Solution

In order to undertake a more intensive study of existing knowledge about the relation between immissions and the destruction of natural stones, quantitative determinations of the immission rates of the pollutants SO_x, NO_x, chloride and fluoride are to be carried out in a number of places with different immission loads.

In the same places and for the same period (1 year), samples of particularly sensitive limestone (Krensheim Muschelkalk) and sandstone (Baumberg sandstone) are to be exposed to the effects of air pollutants. Subsequently the samples so exposed are to be analyzed in the laboratory by means of wet chemical processes as well as modern physicoanalytical methods. The anticipated change in their chemical and physical properties is thus to be described in detail and brought into relation to the immission rate values which will then be available.

The following places are proposed as suitable locations for the measuring and exposure tests:

Place:	Number of measuring stations:	Place:	Number of measuring stations:
France		Greece	
Normandy	1	Athens	3
Paris	2	Delphi	1
Strasbourg	1	Knossos	1
Great Britain		Italy	
London	2	Rome	1
Northern Scotland	1	Sicily	1
		Venice	4

In all these places the measuring stations are to be established on or in the immediate vicinity of objects which are of interest from a conservation point of view, in order to make it possible in

* Excerpts from the proposal as originally presented. The allocation of IRMAs has been revised.

this way to carry out damage assessments also *in situ*.

IV. Implementation

In twenty selected places in Europe, the immission rates of the relevant pollutants causing destruction of natural stone (e.g., SO_x, NO_x, chloride and fluoride) are to be quantitatively determined with the aid of the Immission Rate Measuring Apparatus (IRMA) over a period of one year.

In the same places, moreover, samples of particularly sensitive types of natural stone (sandstone and limestone) are to be exposed for the same period and subsequently are to be analyzed for a change in their properties, so that conclusions may be drawn concerning the reaction processes involved in stone deterioration.

The results so obtained are then to be brought into correlation in order to make it possible to furnish reliable data on the resistance of natural stone objects to varying immission loads or to initiate and apply measures and techniques of passive immission control.

FINAL SITES FOR IRMA MONITORING NETWORK

COUNTRY	LOCATION/MONUMENT
France	Douai
	La Rochelle
	Rouen
	Strasbourg
Great Britain	London
	St. Paul's Cathedral
	Westminster Abbey
	Northern Scotland
	Dunstaffnage Castle
Greece	Athens
	Acropolis
	Temple of Zeus
	Eleusis
Italy	Pisa
	Ravenna
	Rome
	Venice
Netherlands	Delft
	Nieuwe Kerk
	Haarlem
	Lelystadt
	Texel
	Cathedral
Norway	Bergen
	Nidaros Cathedral
Sweden	Floda
	Stockholm
United States	New York
	Bowling Green Custom House
	Federal Hall

Appendix C. VDI Specifications for IRMA

TR-79-0858

VDI GUIDELINES
DETERMINATION OF IMMISSION RATES
DETERMINATION OF THE RELATIVE IMMISSION RATE WITH THE HELP OF THE IRMA PROCESS

Union of German Engineers (VDI)

April 1979
VDI 3794
Sheet 1
Proposal

Translated for EPA by

LITERATURE RESEARCH COMPANY

Annadale, Virginia

VDI GUIDELINES

Union of German Engineers (VDI)	Determination of Immission Rates Determination of the Relative Immission Rate with the Help of the IRMA Process	April 1979 VDI 3794 Sheet 1 Proposal

Preliminary Remarks

1. Fundamentals of the Process

2. The IRMA Device

3. Arrangement and Operation

3.1. Arrangement Out of Doors

3.2. Operation

3.2.1. Beginning of the Measuring Period

3.2.2. End of the Measuring Period

3.2.3. Disturbances

4. Working Instructions

4.1. Harmful Agent Components Determined

4.2. Preparation of the Absorption Solution

4.3. Blind Values

4.4. Processing of the Absorption Solution

4.5. Evaluation of the Analysis Results

4.5.1. Calculation of the Immission or Absorption Rates

4.5.2. Conversion Factor

5. Characteristics Magnitudes of the Process

Literature

VDI Handbook Maintenance of Pure Air

VDI 3794
Sheet 1
Proposal

Preliminary Remarks

During the examination and evaluation of the effects of air impurities on materials we are repeatedly faced with the problem of having to make some type of statement concerning the relationship between the immissions which are present and the effects which they condition. A suitable measuring magnitude is needed for this determination.

Thus, the momentary concentration of harmful agents is generally of less importance than the immission or absorption rate — thus the amount of harmful agent absorbed by the area unit of material per time unit — for the development of harmful effects on materials due to the special effective mechanism. The immission rate is a magnitude which is derived from the measuring magnitude immission dose (ref. 1). Up until now it has not been possible in all instances to determine the specific absorption rate of any given material. In addition to the concentration of harmful agents and the velocity of flow from an intitial direction, boundary layer specific parameters as well as other factors must be included in the measuring magnitude. Therefore, the process described here falls back on a standardized boundary layer as a measuring object. Relative comparisons and statements (e.g., of locality) can then be made.

1. Fundamentals of the Process

In order to determine the relative immission rate with the help of the specific absorption rate of a standard object we use the Immission Rate Measuring Apparatus (IRMA) (ref. 2) which provides such a standardized boundary layer in the form of a liquid surface.

The principle of the process is based on the reaction of the harmful agent which is to be determined with a suitable absorption liquid. The liquid migrates in the form of a cohesive film -- the actual measuring surface -- to the outer side of a cylindrical carrier body which is then additionally saturated.

The contents of the reaction products which are collecting in the absorption solution are related to the standard measuring surface following their determination. The immission or absorption rate is thus calculated in mg · mg^{-2} · d^{-1}. Depending upon the selection of the absorption-liquid, a wide variety of harmful agents can be proven and determined, in some instances when occurring together. Since the solution is continuously circulated by a pump, the well known disadvantages of other summation processes (e.g. lead dioxide candle, Liesegang bell) (refs. 2, 3) are for the most part avoided.

2. The IRMA Device

The measuring device which developed on the principle discussed above is constructed as follows (figure 1)*.

The absorption solution is forced out of 1000 ml supply container (4) into the distributor head (3) by a pressurized hose pump (P). From here it penetrates through the distribution holes and an annular tee-slot (2) into the paper felt of the carrier body (1) which then saturates and wets it uniformly. It then again drips into the supply container from the lower end and begins its circulation over.

An even liquid film is produced on the carrier body in this way; this film corresponds to the geometric surface of the carrier body for all practical purposes. This thus eliminates the influence of the carrier surface and achieves the goal of obtaining a defined standard boundary layer.

The cylindrical carrier body — a normal commercial extraction or Soxhlet casing - is arranged such that it remains for all practical purposes free to

---

* A corresponding device is also manufactured by Gebr. Kless, Worringerstrasse 10-14, 4000 Dusseldorf. Since the pump on this device is supplied by batteries its arrangement is not bound to an available power supply.

the initial flow from the sides. Hindrances in the flow caused by the carrier handles of the distributer head or the supports of the exposure housing (see below) can be neglected according to previous experience from actual practice.

3. Arrangement and Operation

3.1. Arrangement

In order to achieve satisfactory results when the device is set up out of doors it is necessary that the device -- or at least the actual measuring surface -- be protected from the direct effects of rain. In actual practice a simple exposure housing has proved useful for this purpose. This housing is constructed from commercial, galvanized perforated guide rails with a horizontal PVC plate as a protective roof. The device is then mounted directly below the roof surface (Figure 2) so that the height of the device above the ground (this is figured from the middle of the carrier body) is 1400 mm. The exposure housing must be arranged so that it is as free as possible. In the case of surface relevant recordings (e.g. effect cadastres), the distance from trees, buildings, etc. should, if at all possible, be 10 times their height. In the case of relative measurements on buildings, care should also be taken that the arrangement is as free as possible. Since frequent compromises between the ideal measuring site and the technically realizable measuring site must be made in such instances, the peculiarities of the measuring site should be noted in the final report.

3.2 Operation

In practical operation a measuring period of 14 days has proven appropriate. This period is long enough to collect amounts of harmful agents in the absorption solution which are sufficent for dependable analytical determination, and even in the dry summer months sufficient solution remains in spite of the fact that evaporation is more intense.

3.2.1 Beginning of the Measuring Period

After the supply container has been adjusted with the fresh absorption solution and the new Soxhlet casing has been placed on the distributor head, the device is set into operation according to the instructions. The Soxhlet casing is first removed from the bag in which it is sealed as it is being placed on the distributer head. If at all possible contact with the naked hand should be avoided. It is appropriate when operation is begun that the date and time be recorded on the supply bottle as well as in the accompanying report booklet.

After it has been determined for certain that the Soxhlet casing has been saturated and is dripping evenly (after approximately 20 minutes with 5-10 drops/min) the device can be left without additional observation for the normal measuring period of 14 days.

3.2.2 End of the Measuring Period

In order to take into consideration the dead volume of the pump and the supply hoses, the end of the hose which is hanging in the supply container is initially removed while the pump is in operation. It is then necessary to wait until the entire length of hose has been pumped empty (approximately 5 minutes; further details in the operational instructions). Since the silicone material of the hose is hydrophobic there is for all practical purposes no wetting of the interior walls so the pumping it empty without subsequent rinsing is permissible. The casing — again without touching with the naked hand if at all possible - is removed from the distributer head and placed in the remaining solution in the supply container. The date and time are marked on the bottle and in the report and the sealed bottle is transferred to the laboratory for the determination of the harmful agent components which are being sought.

3.2.3 Disturbances

There are generally no disturbances if the maintenance is regular and according to instruction. The operational period of the device is a minimum of 14 days — even at temperatures up to -20°C; in the summer it is 4-6 weeks. If these operational periods are not achieved it is quite certain that the batteries which are used have been stored for excessive lengths of time.

If there are clear or even presumed disturbances, the measured value for the corresponding measuring period should be discarded.

It is also advisable that unusual developments on the casing (e.g. damage, discoloration, dust deposits, etc.) be noted in the report. During the subsequent evaluation unusual measured values which may occur can in many instances be explained in this way.

4. Working Instructions

The working instruction for the further treatment of the contents of the supply bottle can vary, depending on which immissions are to be determined, which absorption solution was used and which analysis procedures are to be used. The instructions which are given here as an example are relevant exclusively to an alkali absorption solution for the determination of acid components; these procedures have previously been used with success in actual practice.

4.1 Harmful Agent Components Determined

The acidic harmful agents containing sulfur which are absorbed in combination by the alkali reaction medium, such as SO_2, SO_3, H_2S and H_2SO_4 aerosols, are considered to be a component sum (SO_x) in the calculations. Thus, we obtain the immission or absorption rate, relative to the standard measuring surface, for SO_x, calculated as SO_2 as a measuring magnitude. In an analagous manner components containing fluorine can be indicated as fluoride, components containing chlorine as chloride.

4.2 Preparation of the Absorption Solution

Necessary Reagents:

Water which is completely free of salts or distilled,
Sodium hydroxide (NaOH), analysis pure,
Ethylene glycol, analysis pure.

The absorption solution which is needed for all of the operational devices within one measuring period is prepared in one mixture. One liter of this solution contains 0.8 g sodium hydroxide and 10% ethylene glycol. The glycol addition slows the evaporation rate considerably in the summer months and in the winter months provides frost protection up to -4°C. An addition of 20% increases the frost stability to -9°C, 30% to -17°C and 40% to -26°C.

One liter of solution is filled into the supply bottle of each device. One Soxhlet casing is also added to each of two additional bottles containing one liter each solution for the purpose of determining the common blind value (double determination). These bottles are removed for the period of the measurements in question and then processed parallel to the measuring solutions.

4.3 Blind Values

Although the chemicals used are analysis pure, the inherent content of relevant components in the solution (blind value) must also be determined. In order to determine the blind values of the Soxhlet casings it is recommended that the blind value sum of the casing and solution be determined together as mentioned in the previous section.

HINT: Since the normal Soxhlet casings do not have the quality of an analytical filter paper, very high blind values can be determined — in the case of chlorides they can even be on the order of magnitude of the measured values. Casings which are stored open can also absorb components of the

laboratory air or perspiration traces from the hands. It is therefore advisable that particularly pure casings which are sealed in polyethylene bags be used. They can be obtained from the Schleicher & Schull firm, Dassell under the name extraction casing 34/150 No. 603 A, or from the manufacturer of the IRMA device. In addition, these casings are characterized by particularly narrow tolerances with respect to their dimensions.

It is also advisable that all of the casings required for one measuring project be obtained from one single manufacturing batch if at all possible.

4.4. Processing of the Absorption Solution

Following the completion of the measuring period, the supply bottles in which the used solution and the used Soxhlet casings have been placed are transported to the laboratory. The beginning and end dates of the measuring periods are first noted for the determination of the measuring time. The casing is then washed out several times with approximately 200 ml of hot distilled water in several portions and the washing water is combined with the solution. This is then filtered into a beaker glass (e.g. with a black filter No. 589 (0 110 mm) from Sleicher & Schull)) in order to remove coarse impurities. It is subsequently evaporated until dry for the quantitative removal of the glycol. The residue is absorbed with 150 ml of distilled water, mixed with 5 ml H_2O_2 p.a. (30%) and boiled. After the H_2O_2 has been boiled off another 2.5 ml of H_2O_2 are added and again boiled off. Any possible silicate precipitate which could develop due to a reaction between the sodium hydroxide and the walls of the beaker glass during the removal of the glycol is filtered off and carefully washed. This is best done in a 100 ml measuring flask. After filling, the solution is ready for the quantitative determintion of the harmful agent contents. If at all possible the corresponding VDI Guidelines should be used for this purpose (refs. 4, 5, 6, 7).

4.5 Evaluation of the Analysis Results

4.5.1 Calculations of the Immission or Absorption Rates

Following the determination, the content of harmful agents in the solution is indicated in the dimensions (mg). After the blind values have been subtracted they must be related to the surface of the Soxhlet casing (standard measuring surface) and the measuring period. The use of conversion factors has proven satisfactory for this purpose in actual practice. The immission or absorption rates are thus calculated according to the formula:

$$\text{Immission rate} \quad [\text{mg} \cdot \text{m}^{-2} \cdot \text{d}^{-1}] = \frac{\text{Factor } [\text{h} \cdot \text{d}^{-1} \cdot \text{m}^{-2}] \cdot \text{Content [mg]}}{\text{Measuring time [h]}} \quad (1)$$

4.5.2 Conversion Factor

The conversion factor is determined by the conversion of the casing surface into square meters and inclusion of the measuring hours in days and is as follows:

$$F = \frac{2,4 \cdot 10^5}{\text{Casing surface } [\text{cm}^2]} \quad (2)$$

The following should be considered a rule of thumb for the surface of the casing: $O = 1,1 \cdot \Pi \cdot D \cdot (L - l)\ [\text{cm}^2]$ (3) in which D = 3.5 cm and L = 15 cm; these are the casing dimensions indicated by the manufacturer. The magnitude l = 0.7 cm is the loss in casing length which is conditioned by the tension device.

HINT: If the casing surface is to be determined more precisely it is necessary to take into consideration the fact that the casings are slightly conical and swell consideraly under the effect of the absorption solution.

The measurements should therefore be done on a casing which has been in contact with the solution for some time and random samples should be taken from time to time. In this connection, and also with respect to the blind values, it is recommended that there be a sufficient supply of casings from the same manufacturing batch.

5. Characteristic Magnitudes of the Process

The characteristic magnitudes of the process are primarly determined by the analysis procedure which is used and can be found in the guidelines cited as examples (refs. 4, 5, 6, 7). For other analysis procedures they should be determined according to the VDI Guidelines 2449 (ref. 8).

LITERATURE

1. Guideline VDI 2450, Sheet 1: "Measuring emission, transmission and immission substances which pollute the air. Concepts, Definitions, Explanations".

2. Luckat, S.: A procedure for the determination of the immission rates of gaseous components. Luft 32 (1972) No. 12, p. 484-486.

3. Leithe, W.: Analysis of the air and its impurities in the free atmosphere and at the work site. Stuttgart: Wissenachaftl. Verlags-Ges. mbH, 1974, 2. Auflage.

4. Guidelines VDI 3795-1 "Determination of immission components in biological material. Determination of the fluorine content in biological samples as well as in IRMA solutions. Photometric Determination".

5. Guidelines VDI 3795-2 "Determination of immission components in biological material. Determination of the fluorine content in biological samples as well as in IRMA solutions. Photometric Determination". (in preparation).

6. Guidelines VDI 3795-3 "Determination of immission components in biological material. Determination of the fluorine content in biological samples as well as in IRMA solutions. Photometric Determination". (in preparation).

7. Guidelines VDI 3795-2 "Determination of immission components in biological material. Determination of the fluorine content in biological samples as well as in IRMA solutions. Photometric Determination". (in preparation).

8. Guideline VDI 2449-1 "Testing criteria for measuring procedures; data sheet on the characterization of analysis procedures for gas immission measurements".

VDI 3794
Sheet 1
Proposal

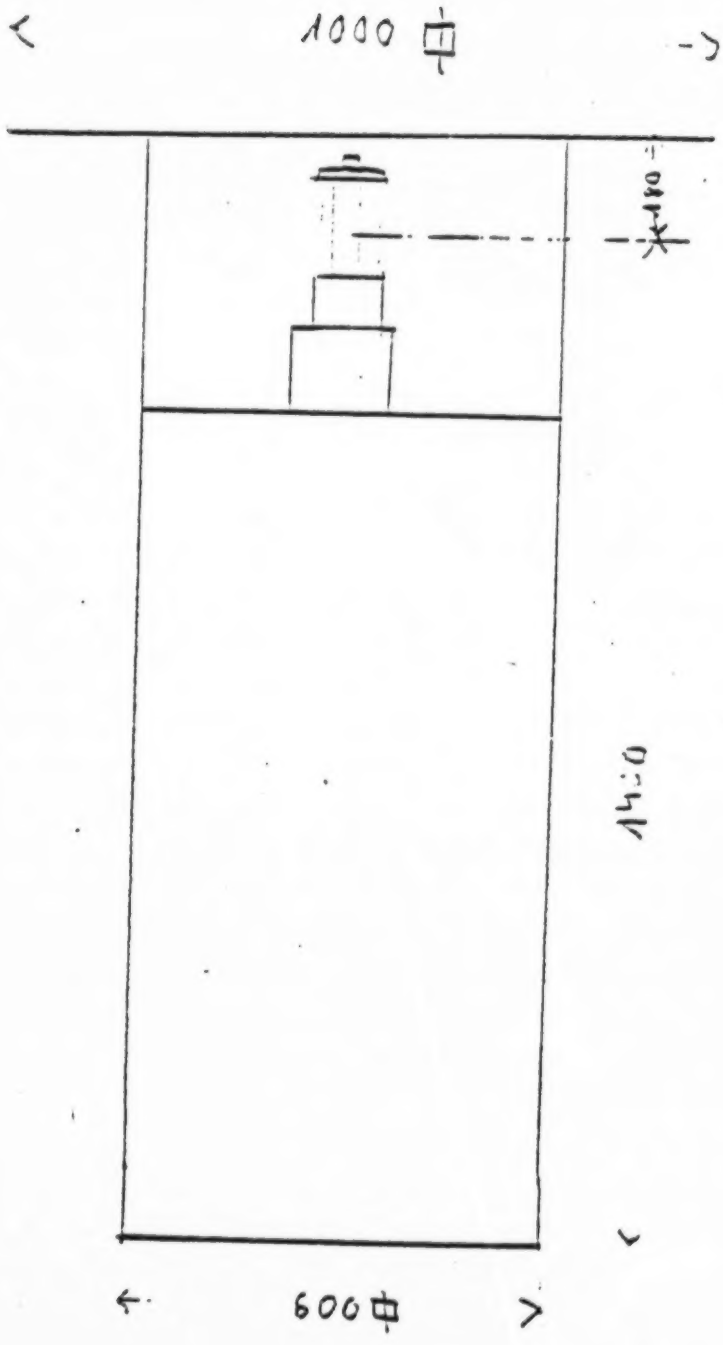


Figure 2

Appendix D. Notes on the Statue of Phoenicia

NOTES ON THE STATUE OF PHOENICIA

by Richard A. Livingston

This report covers several aspects of the Statue of Phoenicia at the Bowling Green Custom house on which the runoff experiments were performed. The first section is the physical description, followed by a section on the statue's history, and finally a description of the marble itself.

I. Physical Description

The statue of Phoenicia stands on the sixth floor cornice on the North or Bowling Green side of the building. The base of Phoenicia is approximately 92 ft above street level. The statue itself is approximately 9 ft tall. The back of the pedestal abuts on to the exterior wall of the building; however, the statue itself is free standing. It also stands out from under any potentially sheltering cornice or overhang.

The statue represents the ancient maritime nation of Phoenicia. It consists of the figure of a woman holding forth a model of a stylized ancient mediterranean ship. The ship is held slightly above waist level and what would have been the inner side of the ship is left attached to the body at this point. Below the ship, the drapery of the statues skirt falls in a number of vertical folds.

The statue has an elaborate headdress, modelled after a head excavated near Carthage. It consists of a tall conical cap flanked on either side by large wheels. The front of the cap and the surfaces of the wheels are covered in patterns of knobs.

On either side of the statue are round columns that extend up to about waist level. These are capped by a series of four rectangles, each smaller than the one below, in order to create a stepped pyramid effect. The columns, decorated in a lotus pattern, are joined to the body of the statue at their inner sides. Below the waist, the back of the statue remains unfinished.

There is no inscription on the pedestal. Moreover, for reasons discussed in the next section, the sculptor's name has been omitted. However, running down the front of the skirt are letters in the Phoenician alphabet spelling out "Bat-Canaan", the name by which the Phoenicians themselves referred to their country[1].

Regarding the present state of the statue, it remains intact, although the presence of large cracks suggest that the rams on the ship may ultimately break off, along with sections of the drapery folds. Several of the decorative knobs on the headdress are absent but this may have occurred during the

original sculpting.

The original pink color of the marble used in the statue can no longer be seen. Most of it is covered by a thin white layer of alteration products. On the areas that are less frequently washed by rainfall, the surface has a dirty greenish color, possibly due to algae. On the sheltered areas of the statue, such as under the arms or the skirt folds beneath the ship, is found a thick black crust or framboidal growth. This consists primarily of a calcium sulfate matrix with particles of fly ash and other urban particulate matter embedded in it.

II. Design and Execution of Phoenicia

It is worthwhile to examine the documentation regarding the history of the statue for clues that could illustrate the process of deterioration. For example, several early photographs exist of the statue (or models of the statue) of Phoenicia at the Bowling Green Custom House(see table I). This suggests the possibility of comparing the present condition of the statue with its original condition in order to obtain an estimate of the rate of damage. Possible indicators of damage in the photographs that could be used include the roughness of the surface or small protruding details of the costume that now appear to be missing.

The history of Phoenicia begins with the basic sculptural program of the row of 12 statues standing on the front facade that was sketched in Cass Gilbert's rendering which won the design competition for the Custom House in 1899[2]. Presumably, Gilbert had already conceived the idea of having them represent twelve leading maritime nations since this would be consistent with the nautical themes that he employed in the ornamentation throughout the building. However, he may not have completed the assignment of identities to all of the individual statues until as late as August, 1903[3].

The commissions for the statues were allocated among prominent American sculptors of the era such as Louis St. Gaudens[4]. While this process was going on, Frederick W. Ruckstull approached Gilbert and appealed to him for one of the commissions[5]. The offer was eventually made on June 12, 1903 for the standard fee of $5000.

Ruckstull was offered the same contract as the other sculptors on the project, but in his case there was a complication because the contract called for all the work to be performed in New York City. Ruckstull was by this time living in France and preferred to do the work there, at his studio in St. Leu Taverny[6]. His counterproposal that the marble block be shipped to France for sculpting was not acceptable to Gilbert.

TABLE 1. PHOTOGRAPHIC RECORDS OF THE STATUE OF PHOENICIA

Record Location*	Description	Date
1. N.Y. Historical Society, Ruckstull File.	6 x 8 Print, full length frontal view of statue	March, 1904
2. The Architectural Record, July, 1906	2 x 4 illustration, retouched, full length 3/4 profile of statue	ca. March 1906
3. Illustration in The Century Magazine, 1906. (Mentioned in Ruckstull ltr. to Gilbert, March 29,1906).	not found	ca. January,1906
4. Documentation of completion (mentioned in J.H. Peirce ltr. to Gilbert, July 9,1906).	not found	July, 1906

*No photographs of Phoenicia were found in the files of the Customs Serviceof the U.S. Treasury or of the Historic Preservation Staff of the General Services Administration. Other photographs may be on file at the Museum of the City of New York or the Cass Gilbert Collection of the Library of Congress, but these have not yet been searched.

The final result was that Ruckstull was permitted to prepare the model in France and it would then be sent to Gilbert for approval. Subsequently, Ruckstull would have to return to New York to carve the statue itself.

The design of the statue required further negotiations. At first, it seems that it was uncertain whether the subject would be Phoenicia or some other maritime nation. After that was decided, Ruckstull apparently had difficulty finding an inspiration[2]. Finally, at a dinner meeting with him in New York on November 4, 1903, Gilbert sketched out a few ideas[7]. This included the statue's pose, the use of columns and modeling the elaborate headdress after the head of a recently discovered Carthaginian statue.

Ruckstull's first sketch (not found) did not please Gilbert because he apparently did not follow instructions regarding the headdress and other details[8]. After a stiff exchange of letters, Ruckstull went ahead and made a 1/3 scale model that incorporated Gilbert's suggestions, including some anachronistic Persian-style horsehead capitals for the columns[9]. The photograph on file at NY Historical Society can thus be identified as being of this model, based on the evidence of the horsehead capitals. This is confirmed by the notation on the photograph indicating it was approved March 26, 1904.

After receiving this approval, Ruckstull proceeded to make the full scale model. His correspondence with Gilbert during this period contains some relevant remarks about the finished condition of Phoenicia. He states that he simplified somewhat the ornamentation of the headdress because the fine details "would certainly be cracked off or eaten away by the weather."[10] He also gave the opinion that the statuary on the Custom House "should not have a high finish...[it] needs sparkling light and shade to make the building sing."[11] In the same vein, he wrote on July 29,1904 that he would "carve it roughly, but with the knowledge of how to get the proper effects 100 feet up."[12] These comments mean that it cannot be assumed that the present rough condition of the statue's surface is the result of air pollution damage. On the contrary, this may simply have been the original condition.

In the letter of July 29, Ruckstull also mentions that he had altered some details in Phoenicia's design. After discussing the matter with a noted French expert on Phoenician antiquities at the Louvre, M. Clermont-Gameau, he felt justified in dispensing with the egregious Persian-style capitals. These were replaced with vaguely Egyptian versions. This evidence implies that the photograph of Phoenicia that appeared in the July, 1906 edition of The Architectural Record, is at least of the full scale model, if not the actual statue itself.

The uncertainty is due to the fact that this photograph was retouched to eliminate the background, so it is impossible to tell whether it was taken in the studio or on the Custom house.

By October 3,1904 the model had been finished and shipped to New York[13]. Ruckstull planned to come over himself as soon as he dealt with some unforeseen personal matters. In order not to delay the work, he authorized a stonecutter named John Grignola of 431 W. 14th St. to begin roughing out the statue prior to his arrival[14].

In the meantime, the marble for the twelve statues on the facade had been ordered from the John M. Ross Marble Co. of Knoxville, Tennessee. A pink variety from the Ross-Republic quarry was specified[15]. The detailed description of this stone is given in the next section. The piece for Phoenicia, a single block measuring 4'2"by 4'4" by 11' was shipped on or about October 21, 1904.[16] Apparently, the marble was sculpted in place on the facade.

Grignola continued to work on Phoenicia through 1905, as a series of further personal matters detained Ruckstull in Europe. Finally, it reached the point where Grignola had carved everything except the final details, most notably the head. Still plagued by personal matters in France, Ruckstull on May 7, 1906 wrote to Gilbert to request that the work be halted until he could come to New York to put on the finishing touches[17]. However, Gilbert, who was already under pressure because of cost overruns and schedule slippages for the entire project[18], decided he could not wait. He authorized Grignola to complete the statue[19] and this was done by July 2, 1906[20].

It is not known whether Ruckstull ever inspected this statue. It may be significant that his name was omitted from Phoenicia while the names of the sculptors of the other 11 statues were inscribed on their creations. At any rate, it would be difficult to say exactly who was most responsible for the finished product: Gilbert, who conceived it; Ruckstull, who made the model; or Grignola, who carved it

The fact that the actual statue was not executed by the sculptor himself may explain why some of the details now appear to be missing, especially on those parts that are not easily inspected, such as the back of the headdress. It is conceivable that working without close supervision, the stonecutter saved labor by omitting details where he thought this would not be noticed. Consequently, one cannot assume that any differences in detail between the original model and the existing statue are the result of weathering. It may simply be due to John Grignola cutting corners.

III. Mineralology and Petrography of the Marble

This section summarizes the extensive material found in Marble Deposits of East Tennessee by William A. Nelson[21]. The marble used for Phoenicia is from the Holston marbles of East Tennessee. This is a major source of marble in this country and has been used in a number of other historic monuments including the Lion statues in front of the New York Public Library and the Morgan bank building. The Holston marbles are fine grained in texture and have characteristic colors ranging from pink to a reddish brown.

The marble for Phoenicia came from the Ross-Republic quarries of the John M. Ross company, located about 4 miles southeast of Knoxville. In the Ross marble, unlike many other Holston marbles, the original structure of bryozoa and crinoid remains has been almost entirely obliterated. The marble is essentially pure calcite with minor traces of dolomite and clay stylolites. The pink color is attributed to hematite. The chemical analysis is given in Table II.

Concerning physical properties, it is moderately coarse-grained, with grain sizes in the range from .12 to .6 mm. It has a specific gravity of 2.7 and a porosity, determined by water absorption, of .3

TABLE II : ANALYSIS OF HOLSTON PINK MARBLE

Lime (CaO)	55.37 %
Magnesia (MgO).....	.13
Manganous oxide(MnO).....	.02
Ferric oxide(Fe_2O_3).....	.21
Alumina(Al_2O_3).....	.15
Silica (SiO_2).....	.16
Sulfur (S)	.01
Loss on Ignition(CO_2 & H_2O).....	43.66
	99.71
Calculated $CaCO_3$ content	98.87

REFERENCES

Key

The abbreviations used are:
CG = Cass Gilbert
FWR = Frederick W. Ruckstull
NYHS/104 = New York Historical Society, Bowling Green Custom House file #104

Unless otherwise indicated all references are to correspondence in the Ruckstull file of the New York Historical Society's collection on the Bowling Green Custom House.

1. FWR to CG, July 29,1904
2. Rendering, New York Historical Society Print #Ng 487-55
3. FWR to CG, August 10,1903
4. Lenard E. Brown (1967) "History of the United States Custom House, 1 Bowling Green, New York, New York.", National Park Service, Division of History, Washington, D.C.,pg.12.
5. FWR to CG, May 19, 1903
6. FWR to CG, July 14, 1903
7. CG, Memorandum to files, November 4, 1903
8. CG to FWR, January 4, 1904, NYHS/104
9. FWR to CG, February 28, 1904
10. FWR to CG, February 22, 1904
11. FWR to CG, July 15, 1904
12. FWR to CG, July 29, 1904
13. John Grignola to CG, October 3, 1904
14. FWR to CG, July 29, 1904
15. William A. Nelson ed.(1924), Marble Deposits of East Tennessee, Bulletin 28, Tennessee State Department of Education, Division of Geology, Nashville, Tennessee, pg. 81.
16. John Peirce to CG, October 11, 1904, NYHS/104
17. FWR to CG, May 7, 1906
18. Lenard E. Brown, op. cit., pg. 2
19. CG, note appended to FWR letter, May 7,1906
20. CG, note appended to John Peirce letter, July 2, 1906
21. William A. Nelson, op.cit.

Appendix E: Specifications for Precipitation Analysis

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

31 OCT 1980

SUBJECT: Acid Precipitation Monitoring

FROM: David G. Hawkins, Assistant Administrator
for Air, Noise, and Radiation

Stephen J. Gage, Assistant Administrator
for Research and Development

TO: Regional Administrators, Regions I-X

There is a growing interest among the States in conducting acid precipitation monitoring. Several Regional Offices have received requests to help fund such monitoring and to provide guidance on the proper techniques to be used. The purpose of this memo is to establish an interim policy for the Agency with regard to providing support to the States for the monitoring of acid precipitation.

First, we should encourage States to move slowly and cautiously in implementing an acid precipitation monitoring program. States which desire to begin new monitoring in the near future should be encouraged initially to focus such monitoring on determining the level of acidity in the precipitation and on establishing long-term trends. This can be accomplished with relatively few monitors located across the State. States should also be advised that there are no new funds available to support acid precipitation monitoring; that such support will have to be negotiated within their existing grants; and that monitoring for at least a ten-year time period should be planned because of the nature of the acid rain problem.

Second, before planning new acid precipitation monitoring, interested States should be encouraged to:

- Determine the type of precipitation monitoring currently being performed in the State. Regions are encouraged to develop cooperative activities with other federally sponsored programs.
- Plan to use a wet/dry sampler but plan to analyze only the wet samples at this time since no acceptable technique is available for analyzing dry samples as yet.
- Collect samples on at least a weekly basis and analyze at a minimum for SO_4^{-2}, NO_3^-, PO_4^{-3}, Cl^-, NH_4^+, K^+, Na^+, Ca^{+2}, Mg^{+2}, total and free acidity or alkalinity, and electrical conductivity.

- Expect a cost of approximately $5,000 per monitor initially, and $5,000 per sampler annually for analysis.

In order to assist you with your acid rain monitoring activities the Environmental Monitoring Systems Laboratory in Research Triangle Park, North Carolina, will undertake the following:

- The development of technical guidelines and a protocol for monitoring.

- The development of a contract for analytical services with a qualified laboratory. States or Regions interested in having samples analyzed through an add-on contract may do so through EMSL.

- The distribution of a limited number of reference samples to a laboratory which a State may designate to perform analyses.

- Continue to operate a national data bank for acid precipitation. All data collected as a result of Agency support must be submitted to EMSL for inclusion in the data bank.

- Provide a clearinghouse for technical questions and assistance in planning for acid precipitation monitoring. Questions and requests for assistance should be directed to the Office of the Director, EMSL, FTS 629-2106.

Additional information will be provided by EMSL-RTP as it becomes available. Should your staff have any questions with regard to this interim policy, please contact Bruce Jordan, FTS 629-5355.

cc: Air and Hazardous Materials Division Directors, Region I-X
Surveillance and Analysis Division Directors, Region I-X